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MAS.330UB Surface Science (2SSt VO, WS 2020/21)

Gruppe

Tag	Datum	von	bis	Ort	Ereignis	Termintyp	Anmerkung
Standardgruppe							
Do	08.10.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	15.10.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	22.10.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	29.10.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	05.11.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	12.11.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	19.11.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	26.11.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	03.12.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	10.12.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	17.12.2020	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	14.01.2021	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	21.01.2021	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	
Do	28.01.2021	16:00	17:30	HS 02.23 (0002020062)	Abhaltung	fix	

1. Introduction

- Historic development
- Definition of the surface
- Ideal and real surfaces (intrinsic/extrinsic defects)
- Nomenclature (Miller indices)
- Ultra-high vacuum (UHV)
- Surface cleaning
- UHV materials (leaks, contaminants)
- Pumps

2. Geometric structure of a surface

- Mathematical description
- Thermodynamics of surfaces (surface tension)
- Facetting
- Crystal surfaces
- Superlattices and reconstructions (Wood and matrix notation)
- Reciprocal lattice
- Experimental determination of surface structures (electron diffraction)
- I/V curves (Bragg condition)
- Adsorption
- Diffusion processes
- Thin film growth (growth modes, energetics)
- Molecular growth processes (self-organization, molecular recognition, binding types)

3. Electronic structure of a surface

- Surface states
- Work function
- Dipole layer
- Smoluchowski effect
- Image potential states
- Experimental determination of electronic structures (Auger electron spectroscopy, photoemission spectroscopy)

4. Microscopy

4.1 Optical microscopy (diffraction limit)
4.2 Super-resolution fluorescence microscopy
4.3 Electron microscopy (TEM and SEM)
4.4 Electron generation, electron optics
4.5 Elastic/inelastic electron scattering
4.6 Secondary electrons, backscattered electrons, Auger electrons, X-rays
4.7 Detection
4.8 Field ion microscopy (field emission and field evaporation)

5. Scanning tunneling microscopy

5.1 Quantum tunneling
5.2 Local density of states
5.3 Sub-Ångström positioning, piezoelectric effect, feedback control
5.4 Vibration isolation
5.5 Tip preparation, sample preparation, molecular deposition methods
5.6 Imaging modes

6. Atomic force microscopy

6.1 Lennard-Jones potential (Pauli repulsion, van der Waals force)
6.2 Force sensors (cantilevers, tuning forks)
6.3 Contact/Non-contact mode AFM

7. General aspects of scanning probe microscopy

7.1 Noise in SPM measurements
7.2 Atomic/molecular manipulation
7.3 Lateral and vertical manipulation
7.4 Single-molecule chemical reactions
7.5 Surface probe spectroscopy
7.6 Selected examples (inelastic electron tunneling spectroscopy, force spectroscopy)
7.7 Spectroscopic mapping
7.8 Applications and recent advances in SPM

Literature:

„Chemistry in two dimensions: Surfaces“
by G. A. Somorjai, Cornell University Press, 1981

„Low energy electrons and surface chemistry“
by G. Ertl and J. Küppers, VCH, 1985

„Physics at Surfaces“
by A. Zangwill, Cambridge University Press, 1990

„Oberflächenphysik des Festkörpers“
by M. Henzler and W. Göpel, Teubner Studienbücher 1991

„Practical Surface Analysis“ (Vol.1+2)
by D. Briggs and M. P. Seah, Wiley, 1992

„Physical Chemistry of Surfaces“
by A. W. Adamson and A. P. Gast, Wiley, 1997

„Surface Science“
by K. W. Kolasinski, Wiley, 2002

„Reactions at solid surfaces“
by G. Ertl, Wiley, 2009

Historic development of Surface Science

1757 **Benjamin Franklin**

Oil-on-water experiment: "I dropped a little oil on the water. I saw it spread itself with surprising swiftness upon the surface... Though not more than a teaspoonful … it spread amazingly and extended … half an acre." (2000 m^2)

Experiment repeated in 1890 by Lord Rayleigh

1833 **Wilhelm Ostwald**

Development of the heterogeneous catalysis

Nobel prize in Chemistry 1909 *"in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction"*

1870-ies **J. W. Gibbs**

Thermodynamical aspects of surfaces

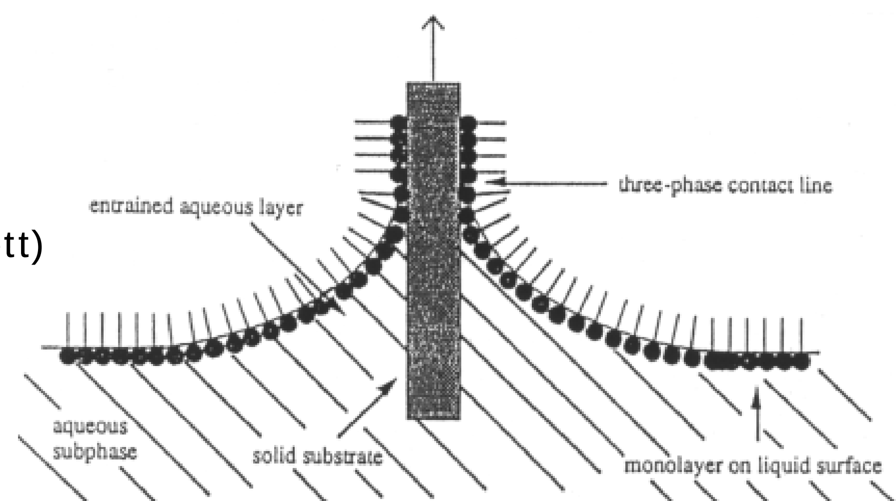
1917 **Irving Langmuir**

Study of thin oil films (term „monolayer")

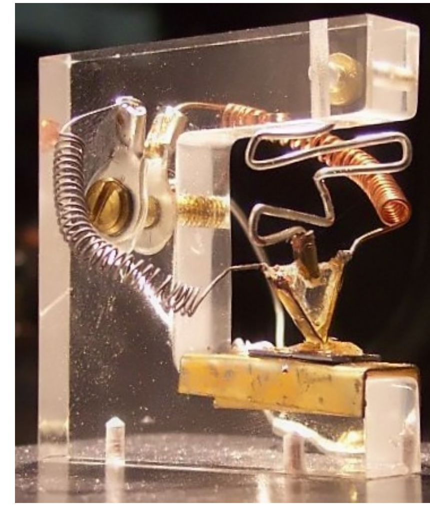
„Langmuir-Blodgett films" (with K. Blodgett)

Nobel prize in Chemistry 1932

"for his discoveries and investigations in surface chemistry"



Historic development of Surface Science



1949 **W. B. Shockley, J. Bardeen, W. H. Brattain**
Study of electronic surface properties

Nobel prize in Physics 1956 *"for their researches on semiconductors and their discovery of the transistor effect"*

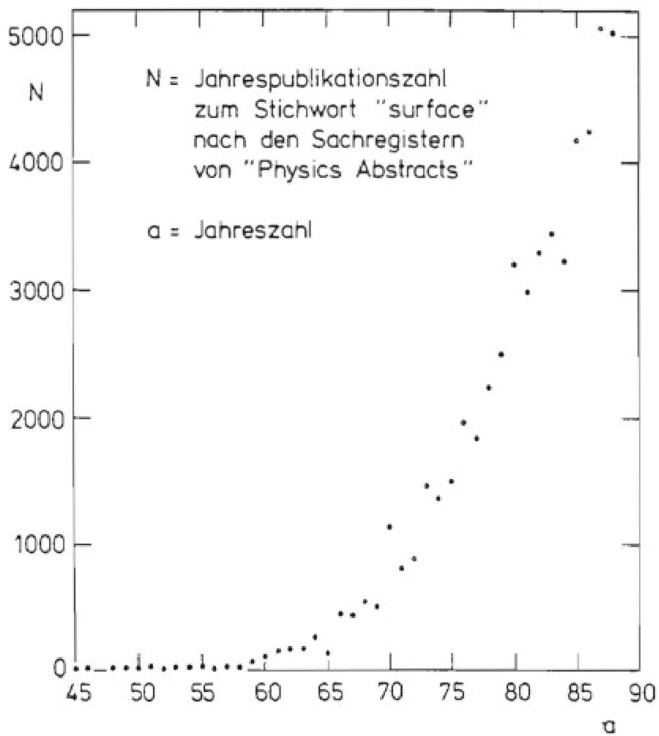


Abb. 1: Jahrespublikationszahl 1945–1988 nach Nennungen zum Stichwort „surface" in den Stichwortverzeichnissen von PHYSICS ABSTRACTS.

1950-ies Development of commercially available materials for ultrahigh vacuum („space race")

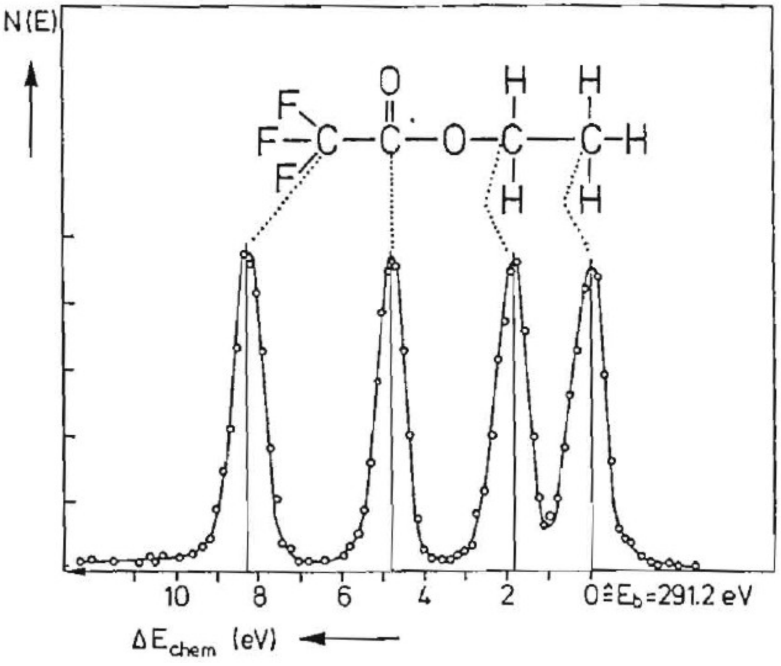
Surface science methods under vacuum conditions developed rapidly

Historic development of Surface Science

1960-ies **Kai Siegbahn**

Development of ESCA
(electron spectroscopy for chemical analysis)

Nobel prize in Physics 1981 *"for his contribution to the development of high-resolution electron spectroscopy"*

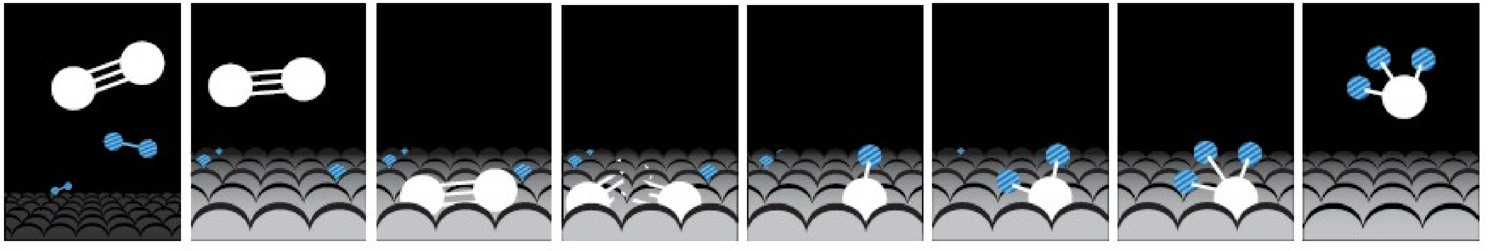


since 1970-ies

Gerhard Ertl (Fritz-Haber-Institut Berlin)

Nobel prize in Chemistry 2007 *"for his studies of chemical processes on solid surfaces"*

Haber-Bosch process: $N_2 + 3H_2 \rightarrow 2NH_3$ (in the presence of an iron catalyst)



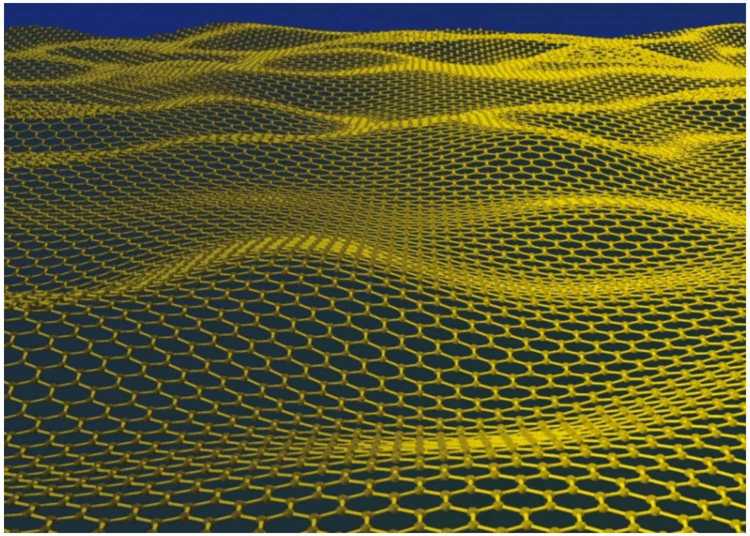
In the Haber-Bosch process nitrogen (white) reacts with hyrogen (striped) on an iron surface to then form molecules of ammonia which are released from the surface. This reaction, which extracts nitrogen from air, is an important step in the production of artificial fertilizer.

Historic development of Surface Science

2004 **A. Geim and K. Novoselov**
Separation and characterization of single graphene sheets (Graphene is „only surface“)

Nobel prize in Physics 2010 *"for groundbreaking experiments regarding the two-dimensional material graphene"*





Surface Surface is very interdisciplinary
(rather Surface Science than Surface Chemistry or Surface Physics)

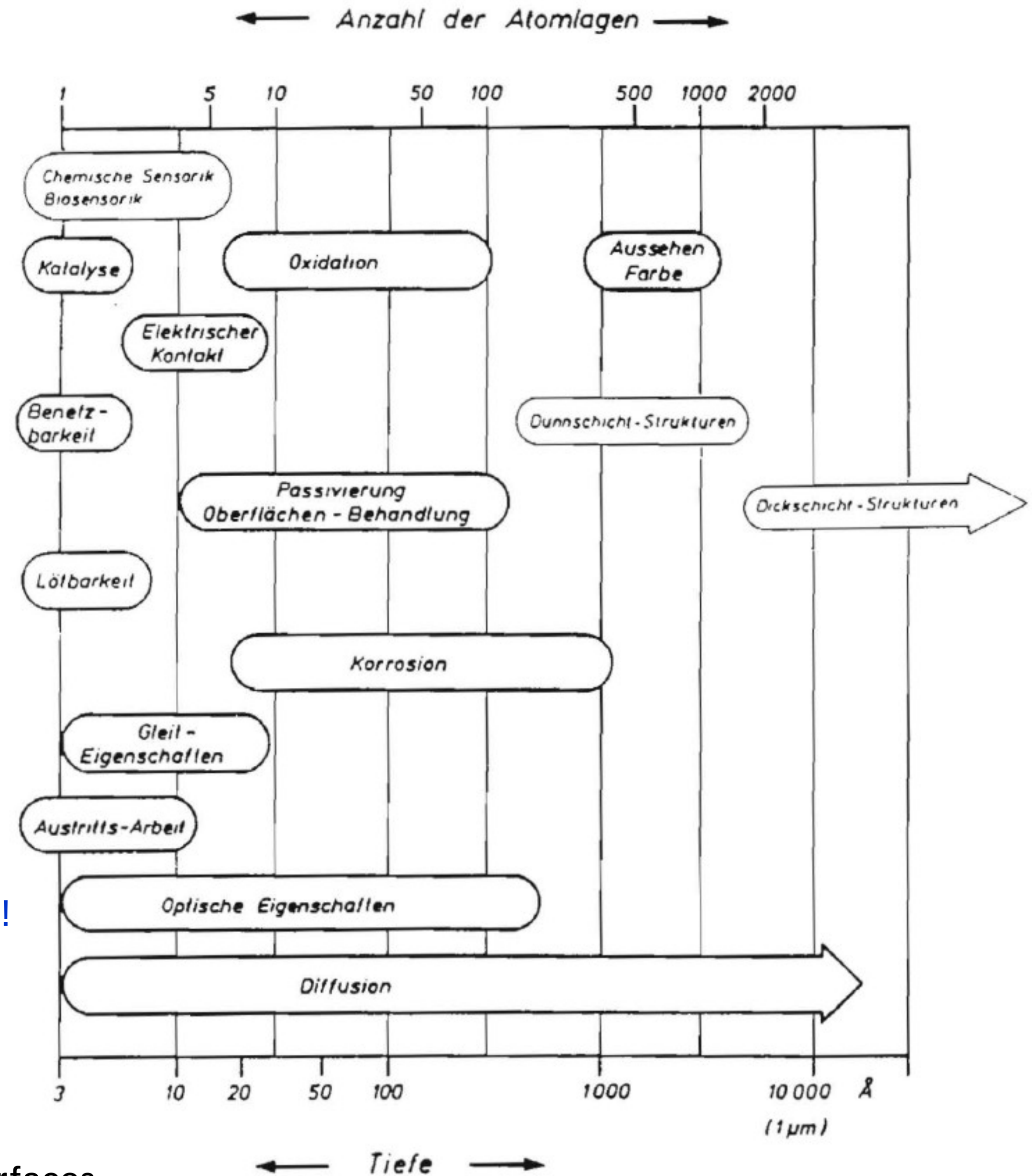
- Physics (e.g. electronic and optical properties)
- Electronics
- Chemistry (e.g. catalysis)
- Molecular Science
- Material Science (e.g. friction, corrosion)

What is a surface?

Surface = Interface between a solid and a liquid/gas/vacuum

Thickness?

…depends on the transition to the bulk properties (defects, periodicity,…)
The surface is not perfectly 2D, but has a finite thickness
…depends on the property that is described



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

Most properties are defined by rather few layers!

Interest:
- Model systems for phenomena at surfaces/interfaces
- Important in applications (catalysis and thin films)
- Interest in processes ON the surface (which acts as a supporting layer)

Why is ultrahigh vacuum (UHV) needed?

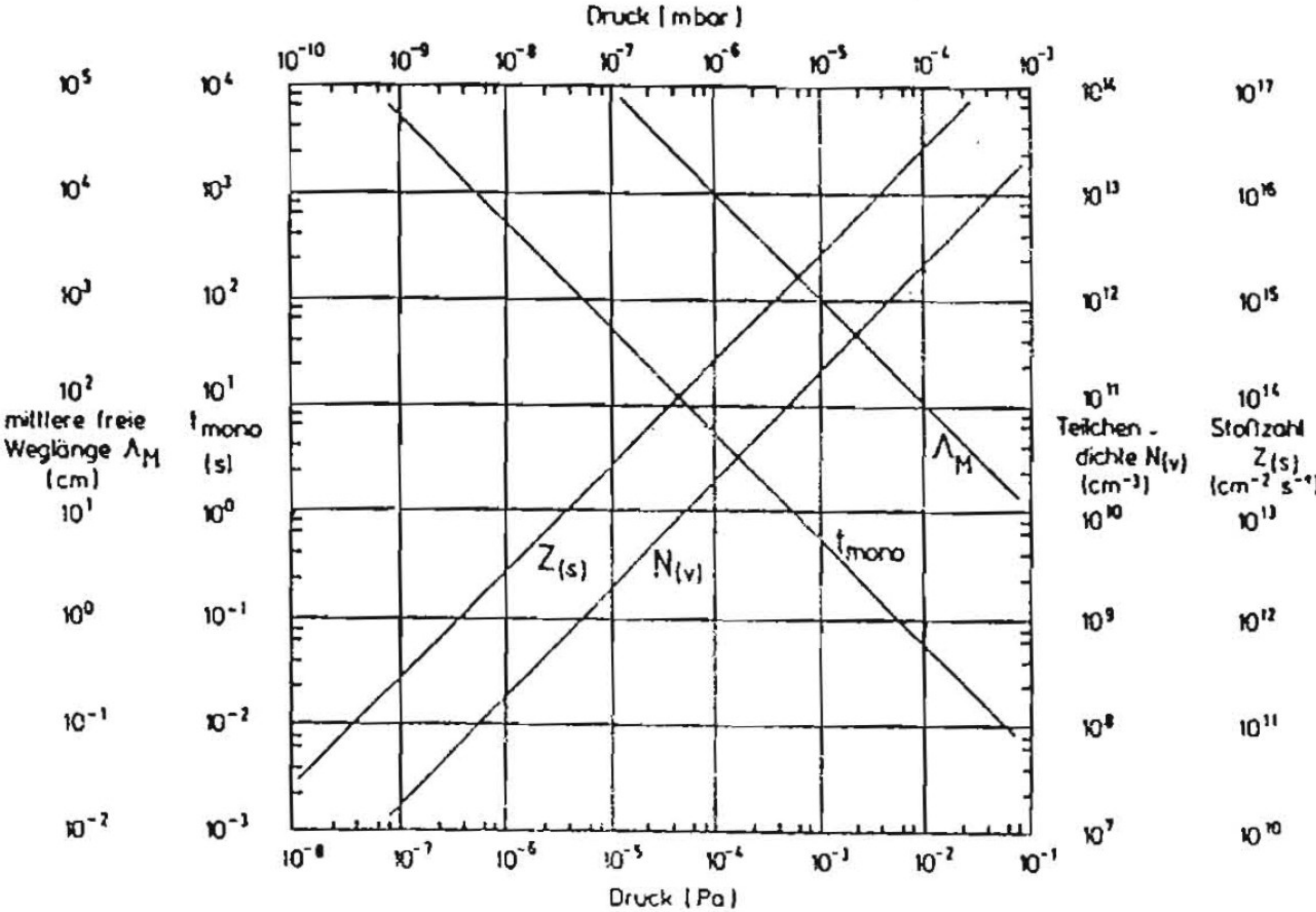
Consider a surface under atmosphere: particle speed given by Maxwell-Boltzmann distr

…from there follow:
Z(s), Λ_M and t_{mono}

At high pressures:
1) Very quick coverage of a monolayer
2) Low mean free paths (bad for particle beams)

(Sticking coefficient of 1 is realistic?)

Temperature defines desorption and adsorption



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

How to obtain clean surfaces

- Cleaning: 1) Ion sputtering
  2) Annealing

- Cleaving under UHV (good for very reactive surfaces)
- Film growth under UHV (thin films have bulk properties)

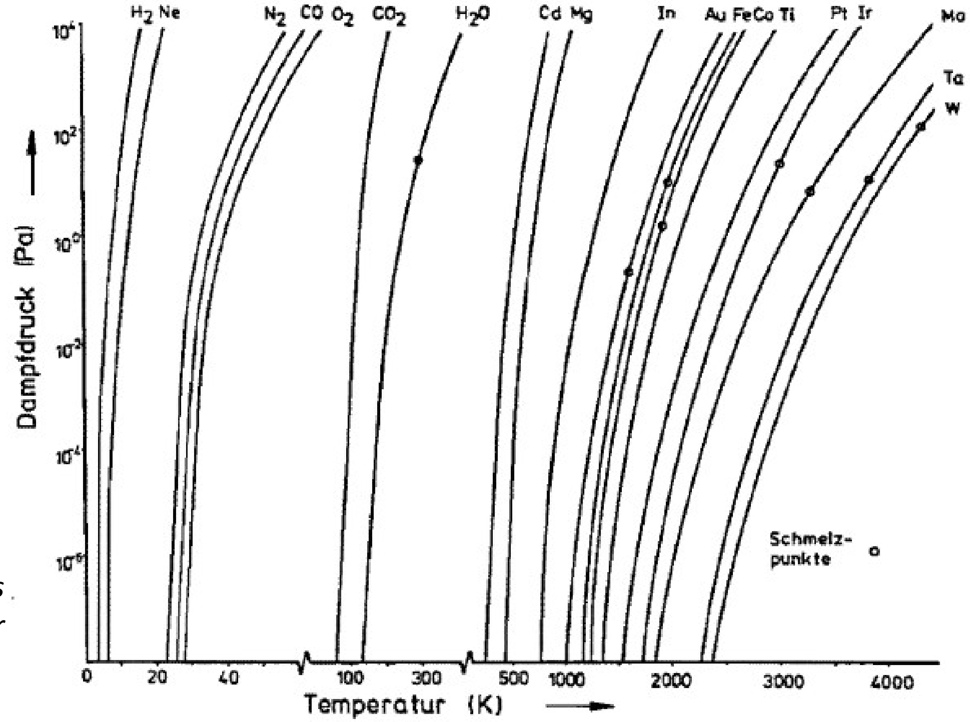
UHV materials

- Careful choosing the chamber material (low partial pressure)

- Air gases (N2, O2, etc.) are no problem, water is

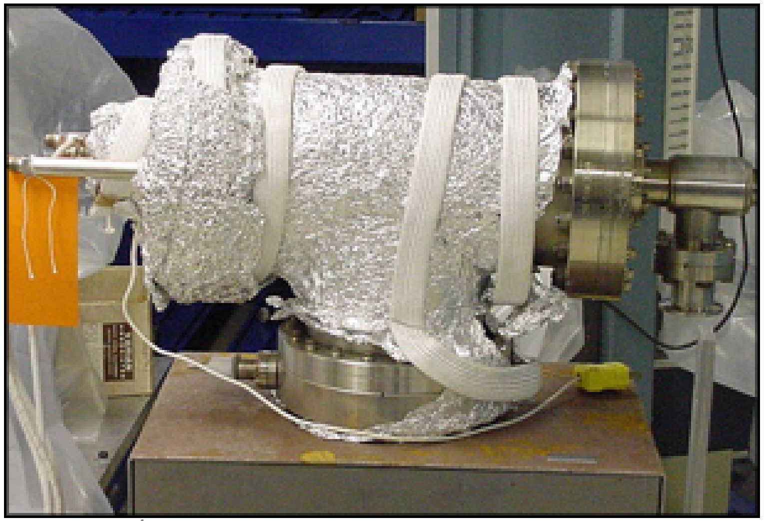
- Flanges and windows (Cu gaskets)

- Bake-out (water!)



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

Briggs/Seah, Practical Surface Analysis



NSLS: National Synchrotron Light Source

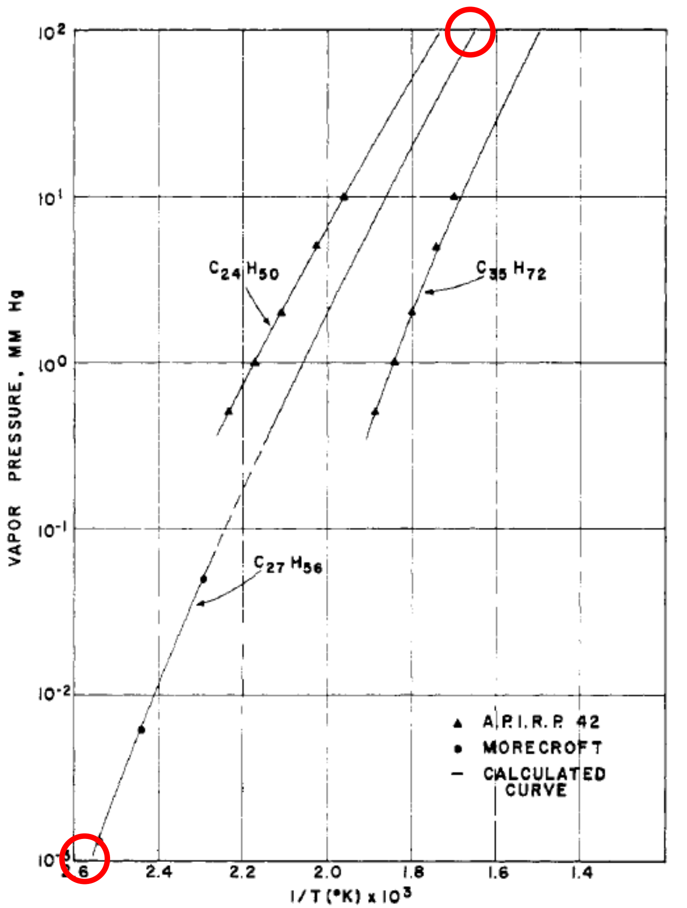
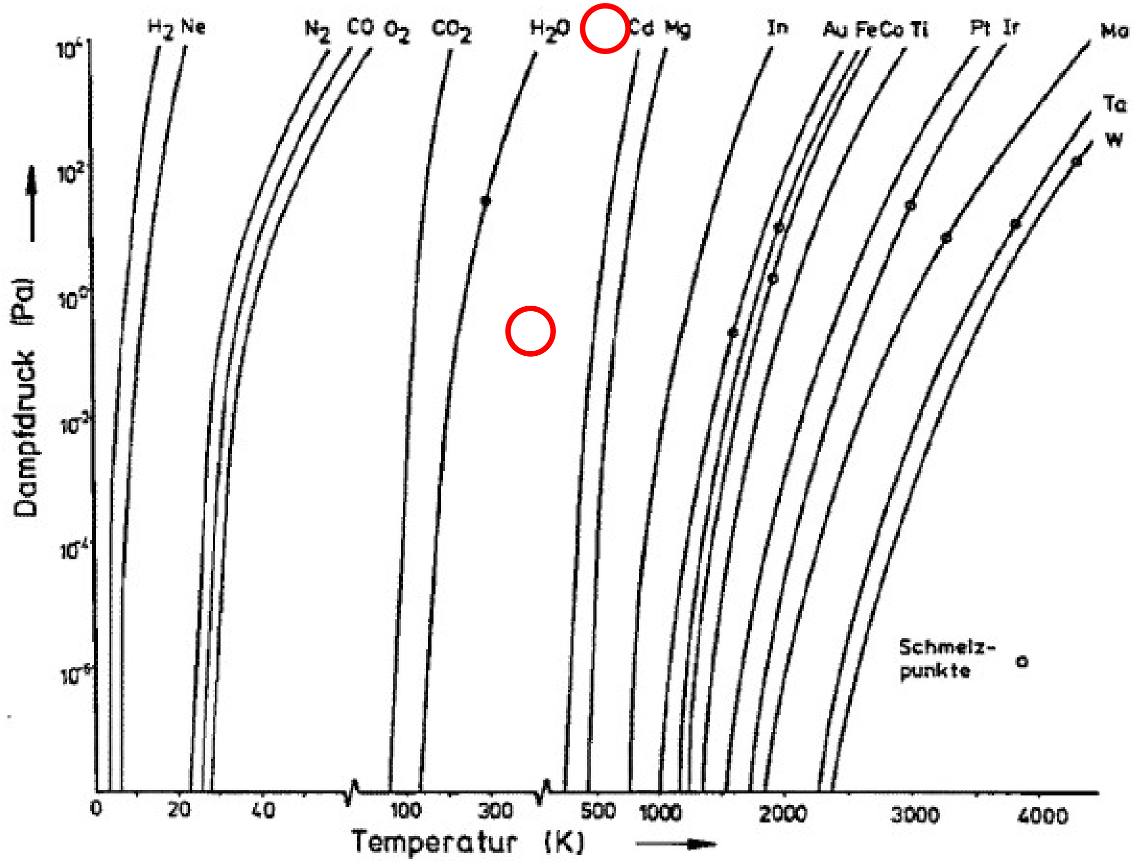


Figure 1. Comparison of predicted and experimental lo pressure data for three normal alkanes

A. P. Kudchadker and B. J. Zwolinski
J. Chem. Eng. Data 11, 253 (1966)



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

Pumps

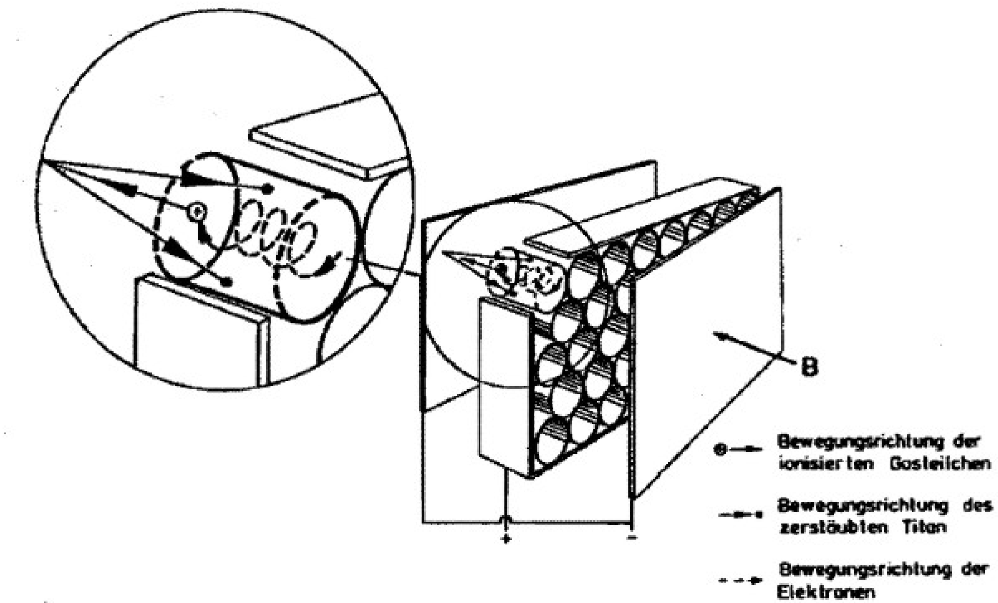
Rotary pump: Atmosphere to 10^{-3} mbar

Turbomolecular pump: 10^{-2} mbar to 10^{-10} mbar

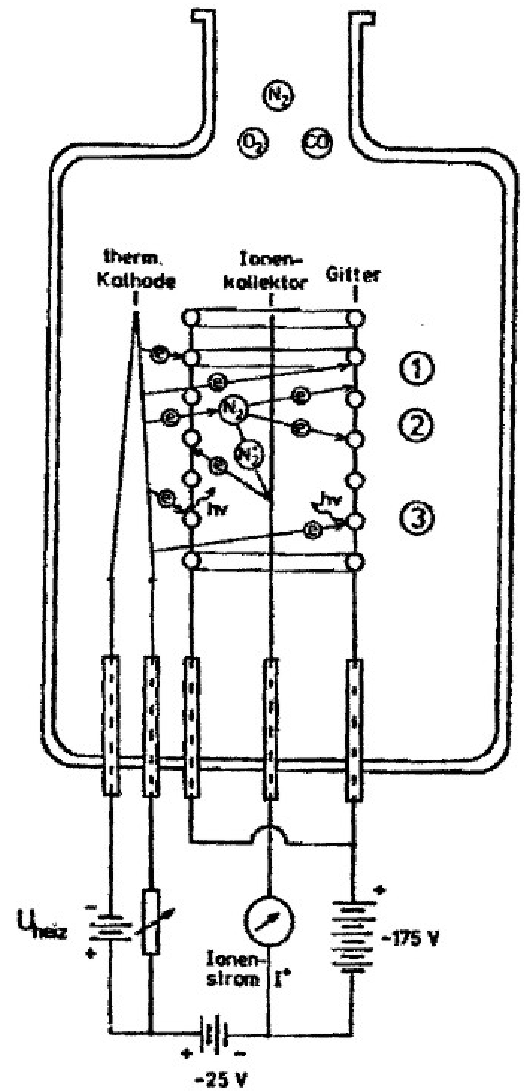
Iongetter pump: 10^{-5} mbar to 10^{-11} mbar

Titanium sublimation pump: 10^{-2} mbar to 10^{-11} mbar

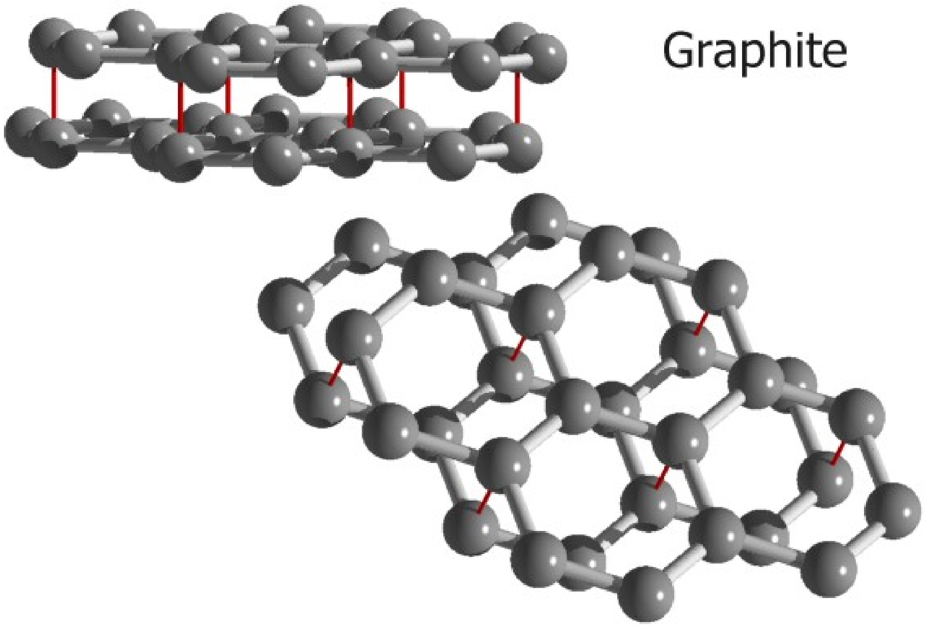
Iongetter pump

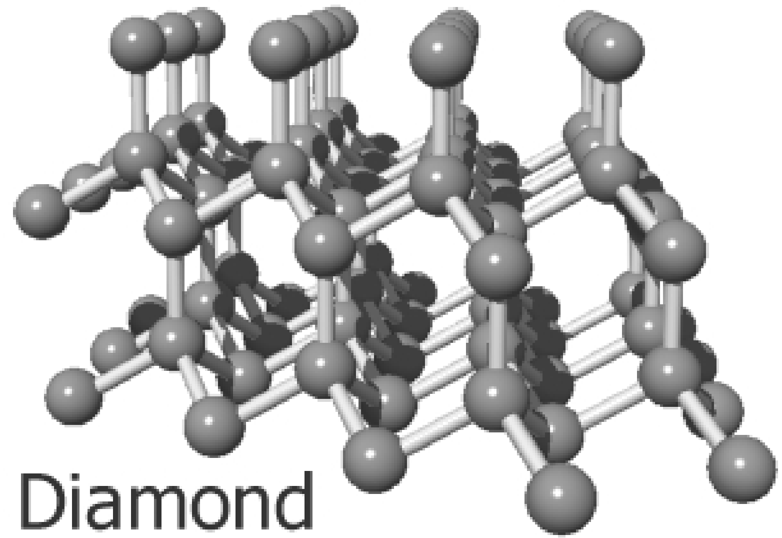


Pressure measurement



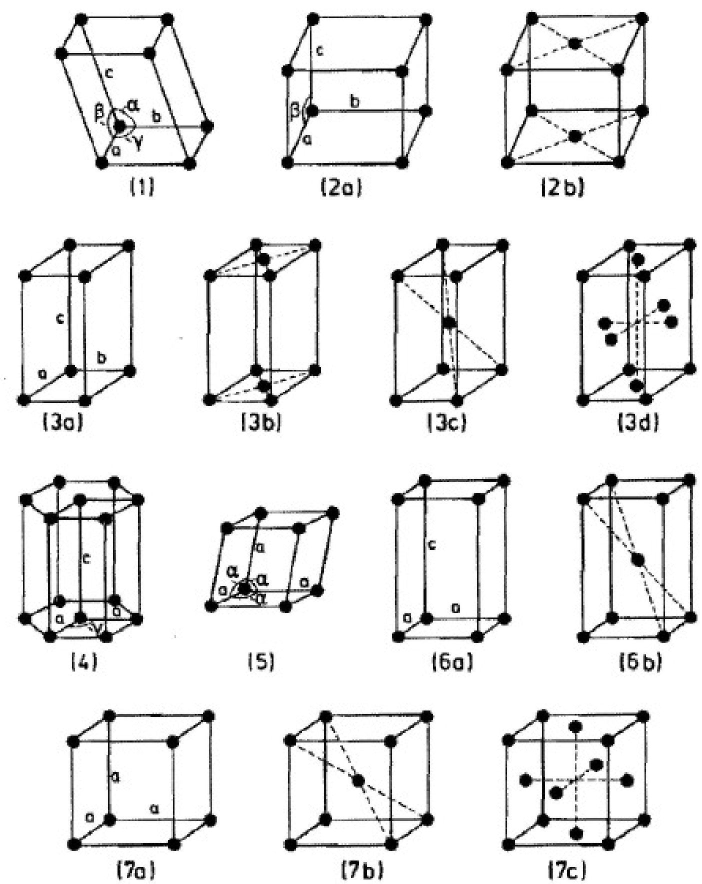
Graphite vs. Diamond



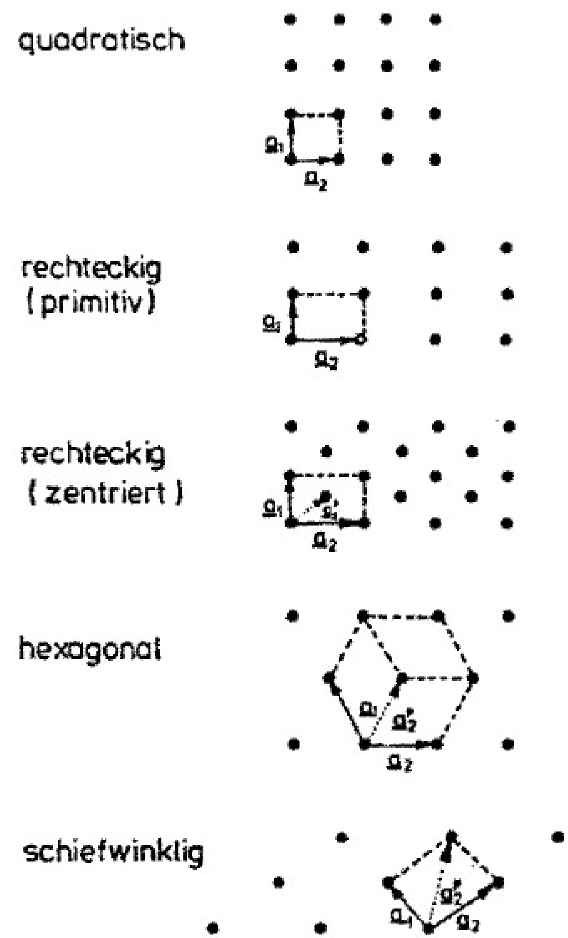


Surface lattices

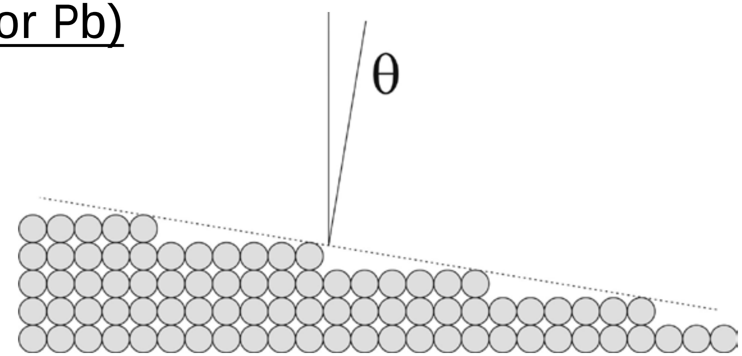
14 Bravais bulk lattices

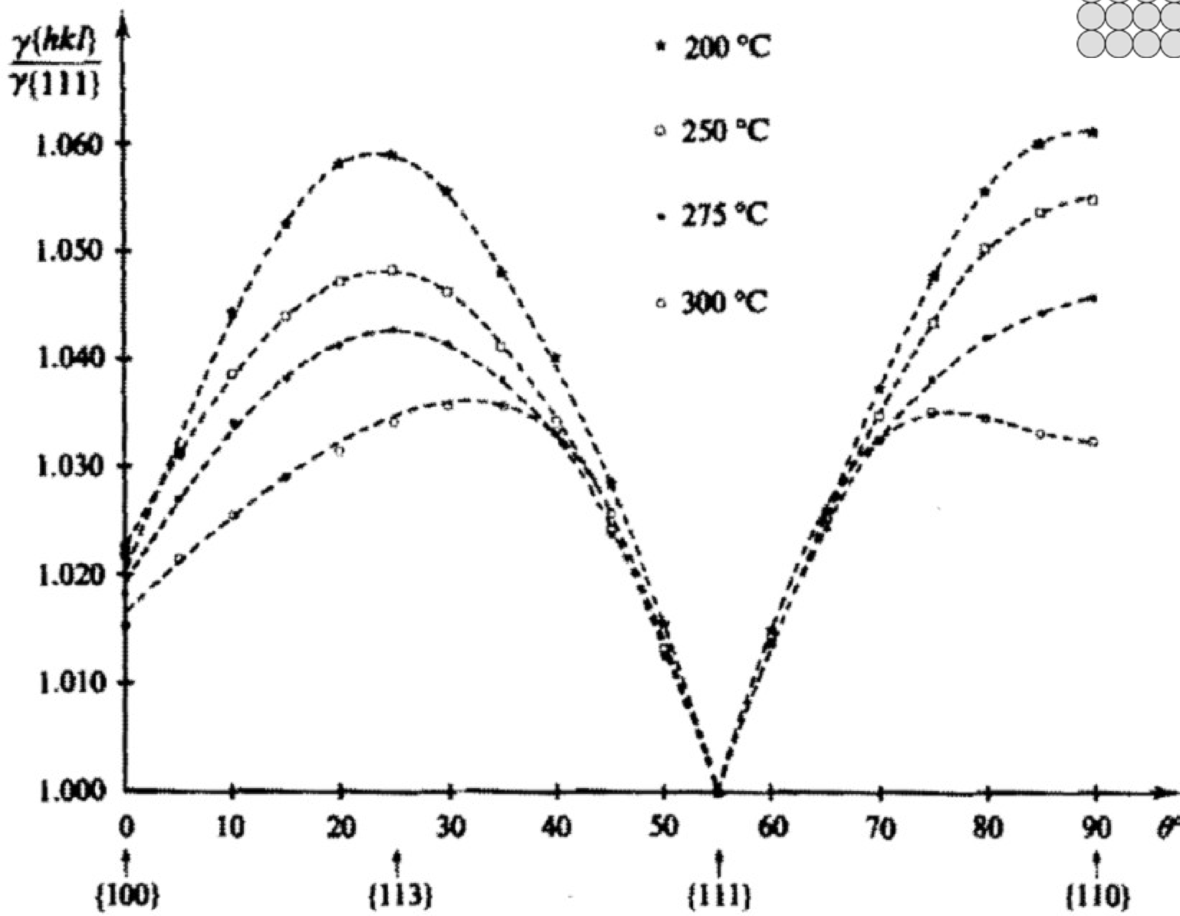


5 Bravais surface lattices



Surface free energy for different orientations (for Pb)





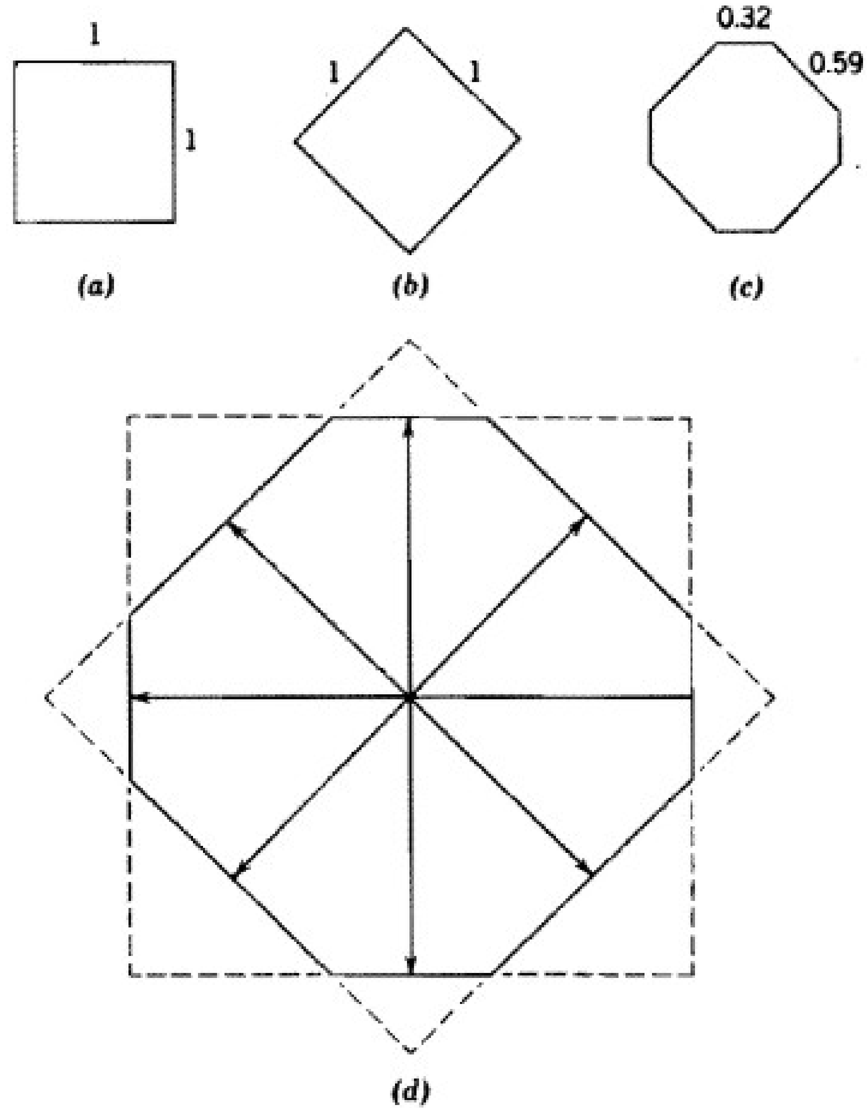
Zangwill: Physics at Surfaces, Cambridge

How does solid matter crystallize?

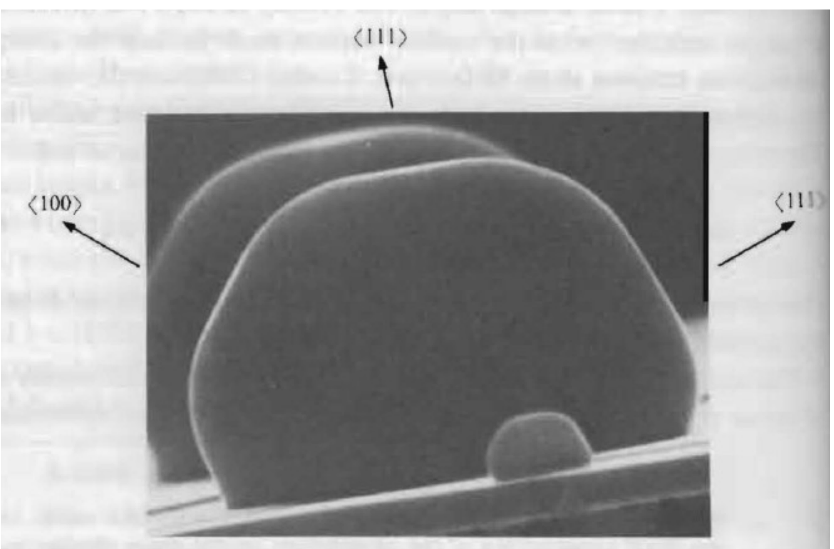
Wulff construction (1901)

Total surface free energies for a 2D crystal of 1 cm^2 area:

(a) Only (10) planes: 1000 ergs (=10^{-4} J)
(b) Only (11) planes: 900 ergs
(c) Combination of both: 851 ergs



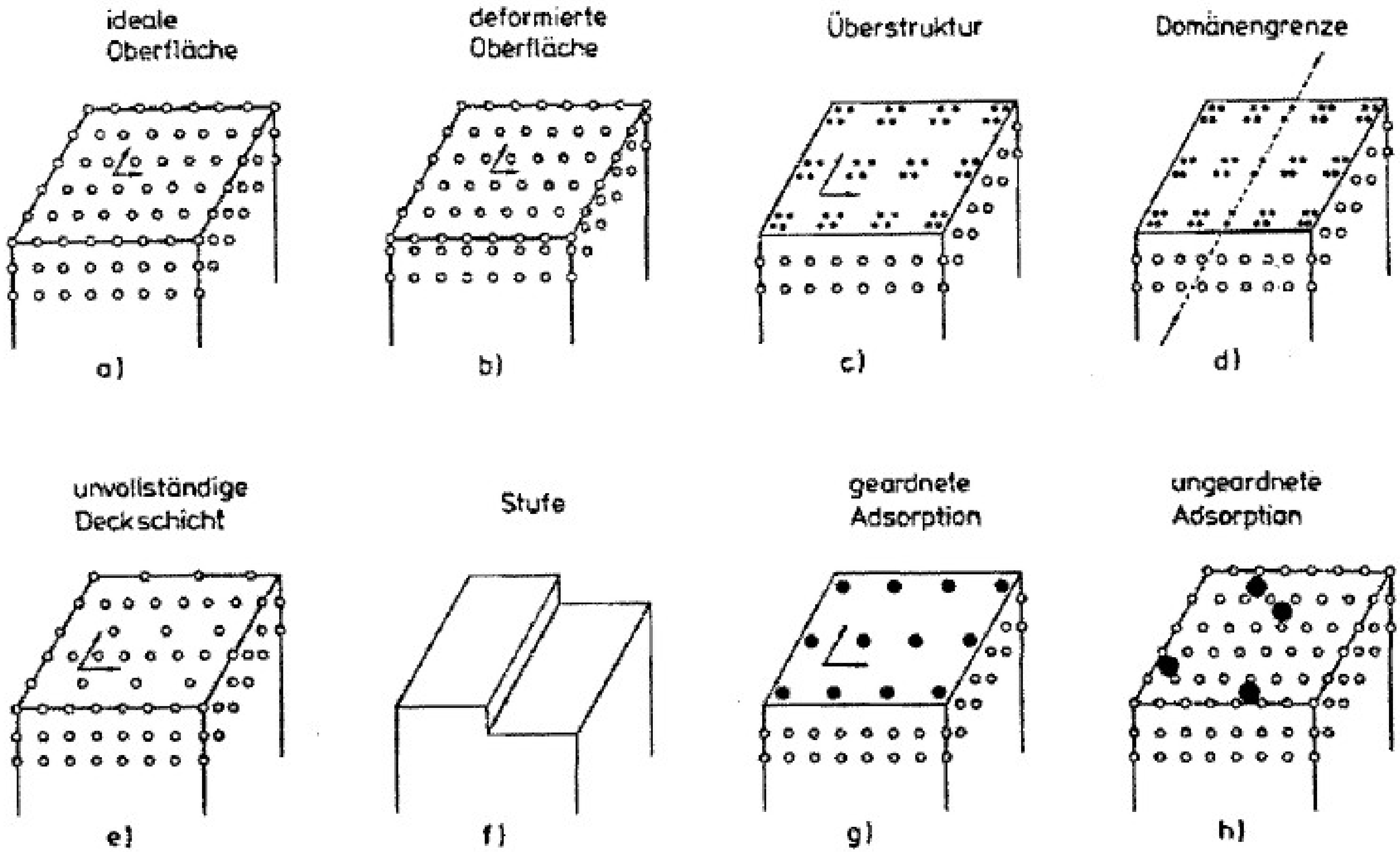
Pb crystal (image size ≅ 5 x 7 μm^2)



Adamson/Gast: Physical Chemistry of Surfaces, Wiley

Zangwill: Physics at Surfaces, Cambridge

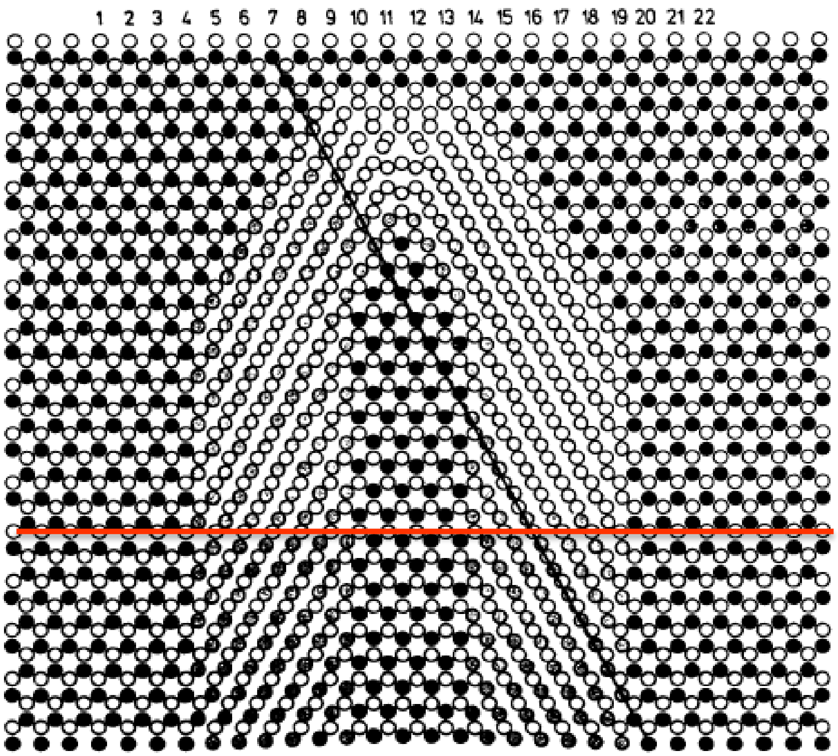
Geometric structure of surfaces



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

Examples of surface reconstructions

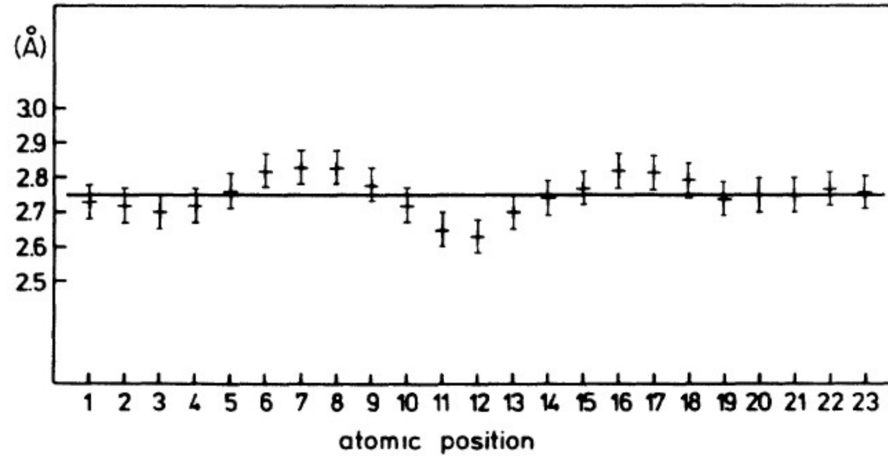
Au(111) „Herringbone reconstruction“
(22x√3)



● First layer
○ Second layer

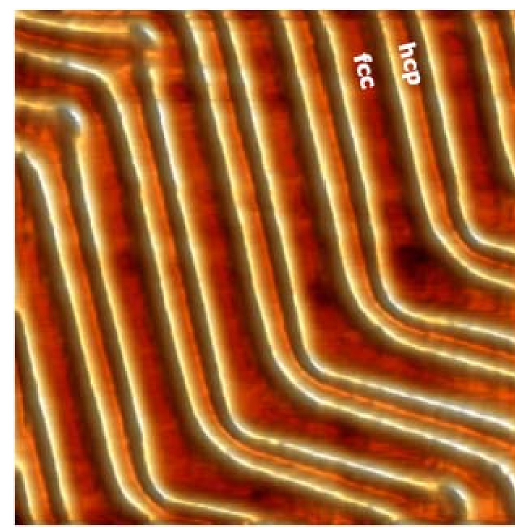
fcc area **hcp area** **fcc area**

transition area transition area



J. V. Barth et al., Phys. Rev. B 42, 9307 (1990)

36 x 36 nm^2



J. Kröger et al., New J. Phys. 9, 153 (2007)

Dichte Kugelpackung

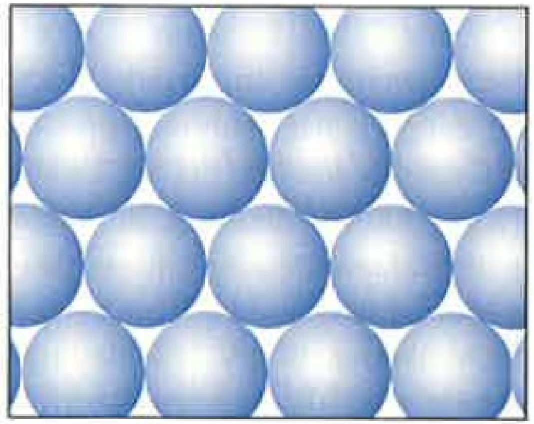


Abb. 20-32 Die erste Schicht von dicht gepackten Kugeln, die zum Aufbau einer dreidimensionalen dicht gepackten Struktur dient.

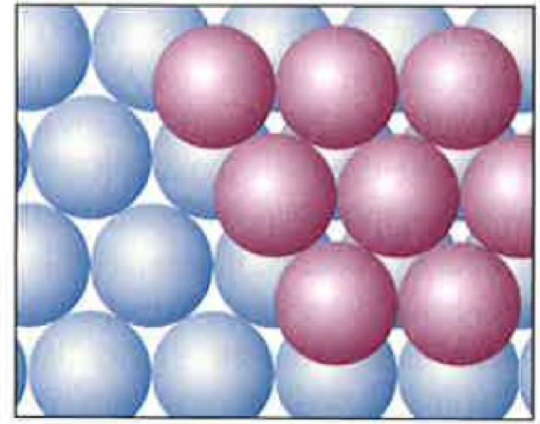
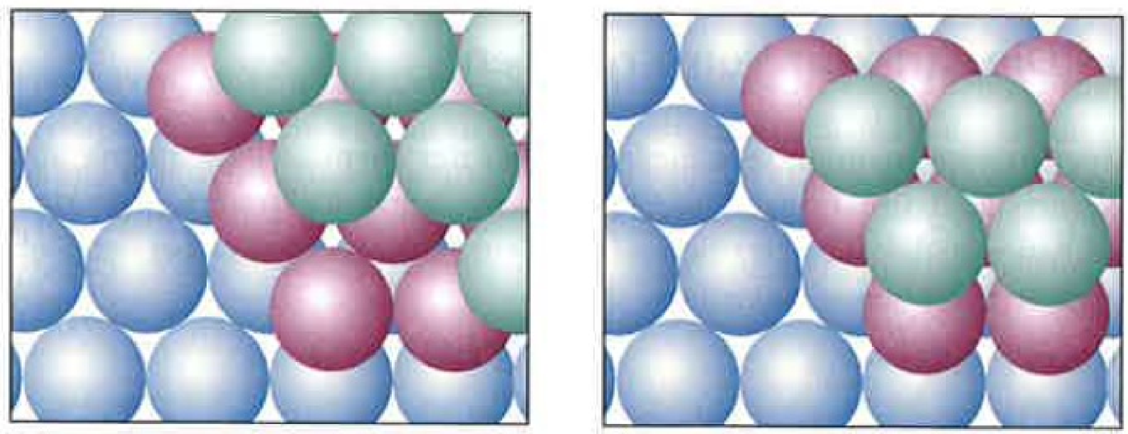


Abb. 20-33 Die zweite Schicht dicht gepackter Kugeln liegt über den Vertiefungen der ersten Schicht. Diese beiden Schichten bilden den AB-Teil der dreidimensionalen dichten Kugelpackungen.



(a) (b)

Abb. 20-34 (a) Die dritte Schicht aus dicht gepackten Kugeln kann über den Lücken der zweiten Schicht liegen, die direkt über den Kugeln der ersten Schicht liegen. Man erhält so die Schichtfolge ABA, die einer hexagonal dichten Packung entspricht. (b) Stattdessen kann die dritte Schicht auch in den Lücken der zweiten Schicht liegen, die nicht über den Kugeln der ersten Schicht liegen. So entsteht die Schichtfolge ABC, die einer kubisch dichten Packung entspricht.

Source: Atkins/de Paula, Physikalische Chemie

Examples of surface reconstructions

Pt(100)

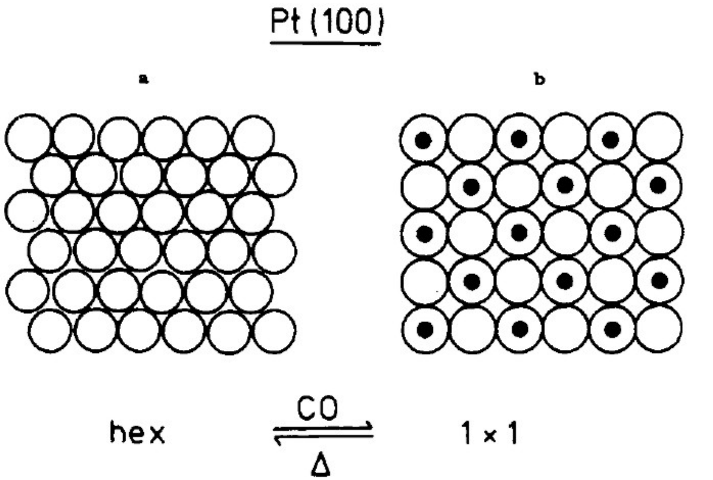
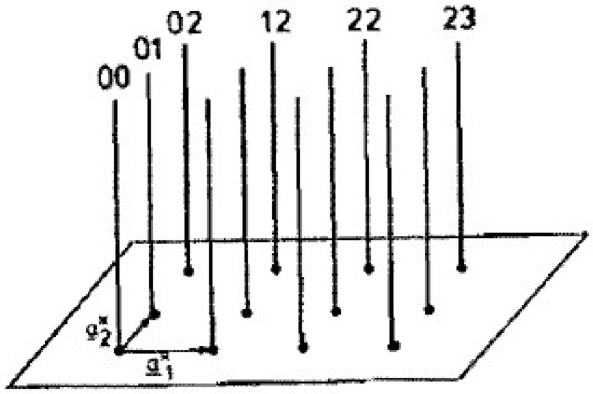
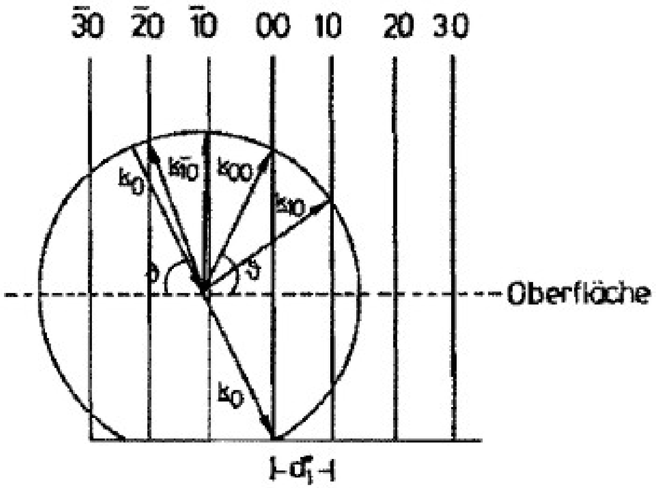


Figure 14. The clean Pt(100) surface is reconstructed and exhibits a quasi-hexagonal configuration of the atoms in the topmost layer (a). Adsorption of CO lifts this reconstruction and causes the formation of a $c2\times2$–1×1 structure (b).

G. Ertl, Langmuir 3, 4 (1987)

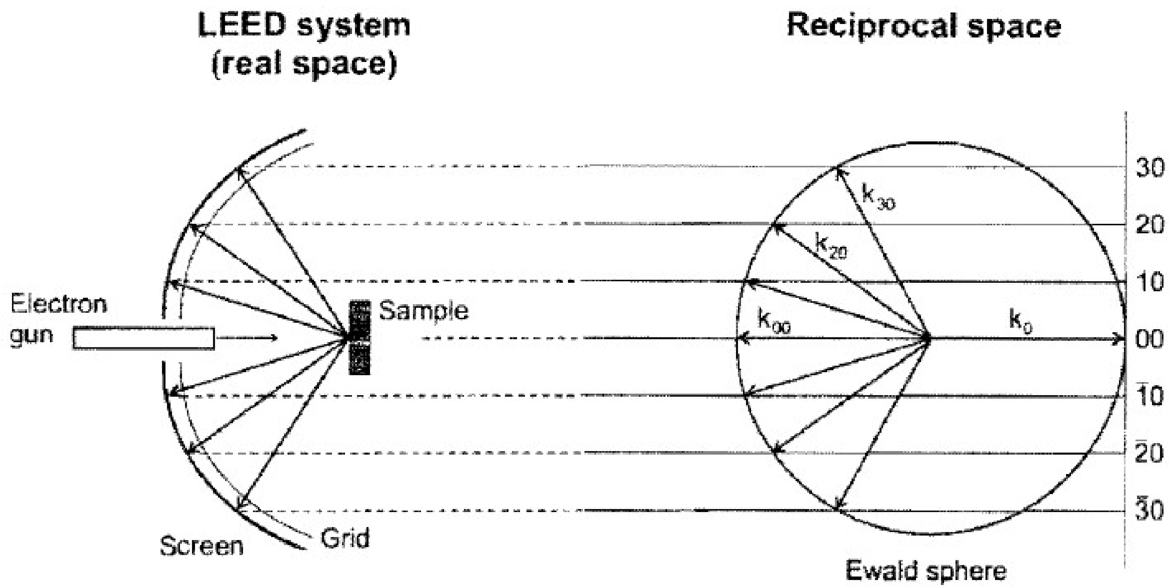
Reciprocal space of the surface

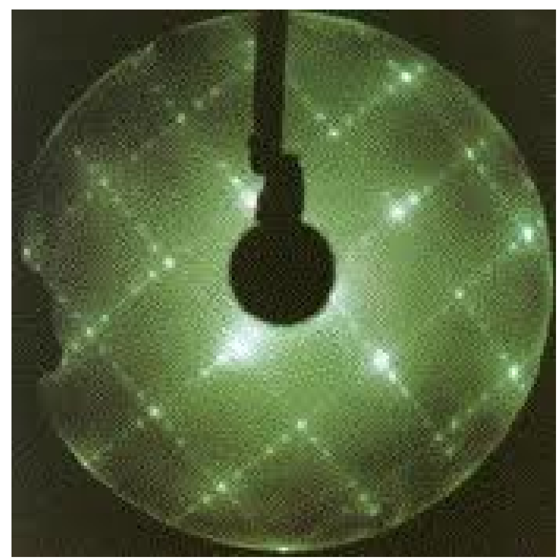




Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

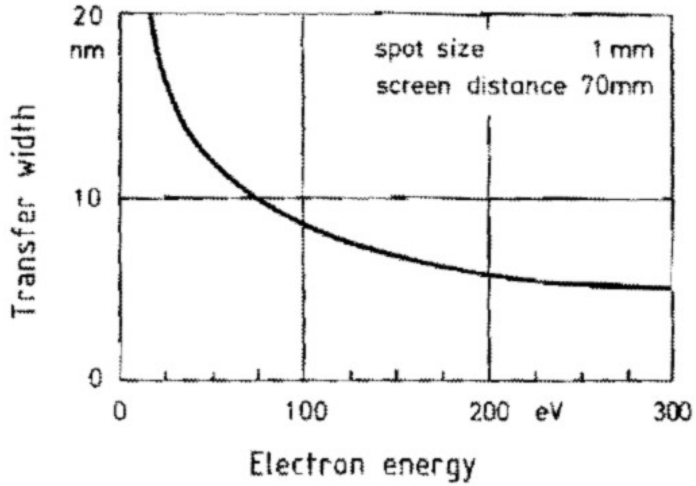
LEED (low energy electron diffraction)





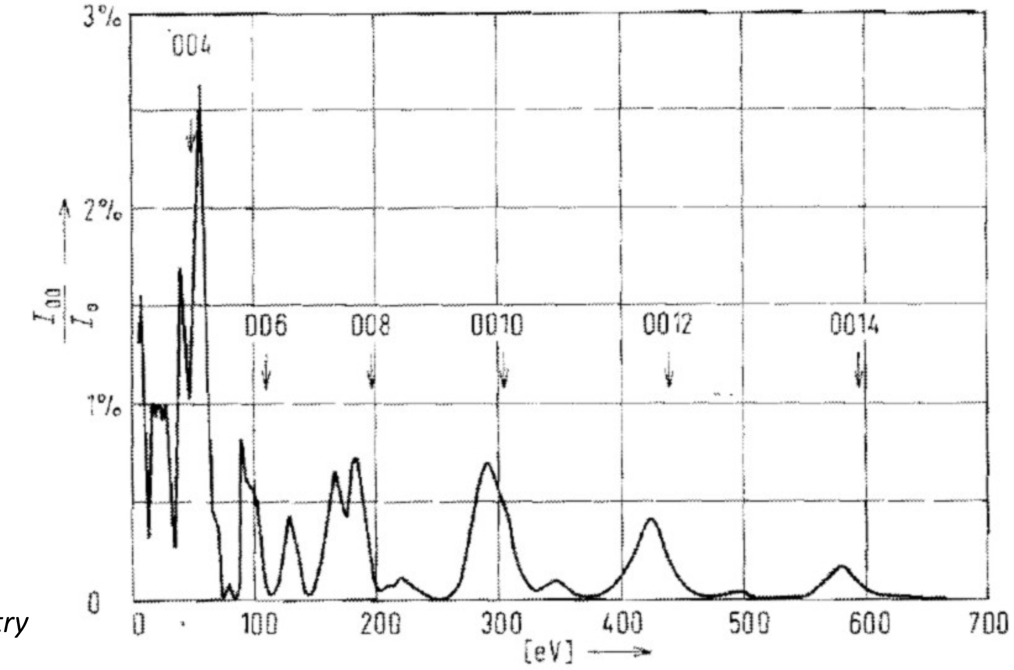
LEED

Transfer width



Ertl/Küppers: Low Energy Electrons and Surface Chemistry

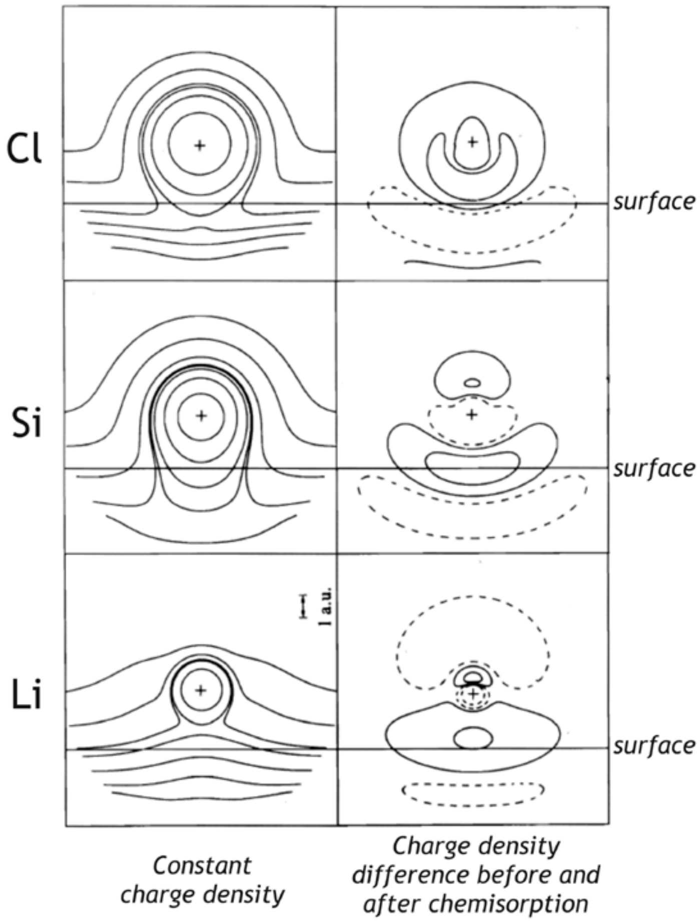
I/V LEED



Ertl/Küppers: Low Energy Electrons and Surface Chemistry

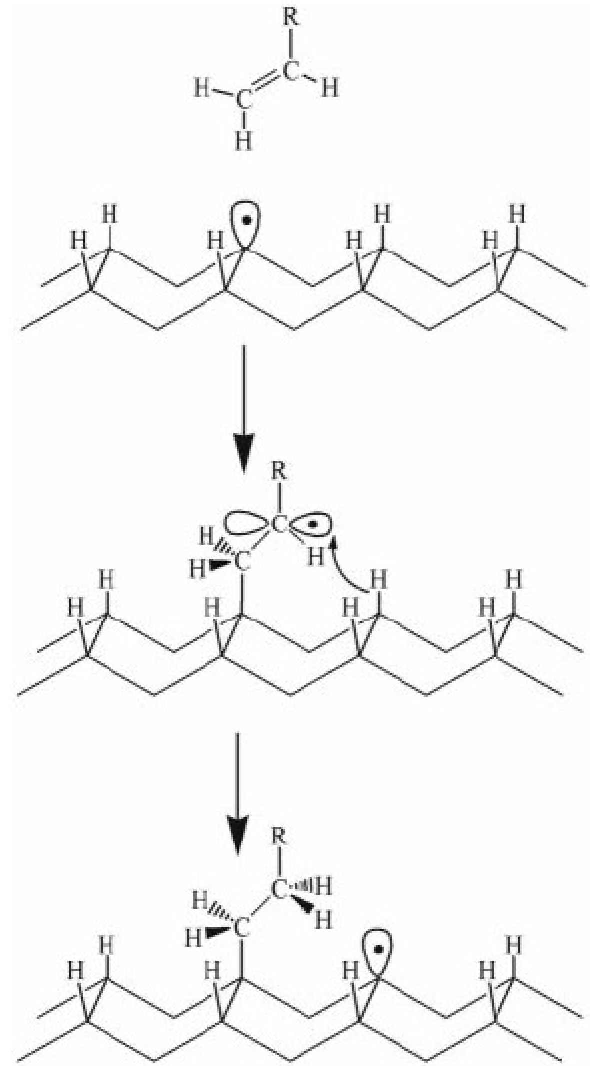
Chemisorption

Chemisorption of atoms on
Al (calculation – Jellium model)



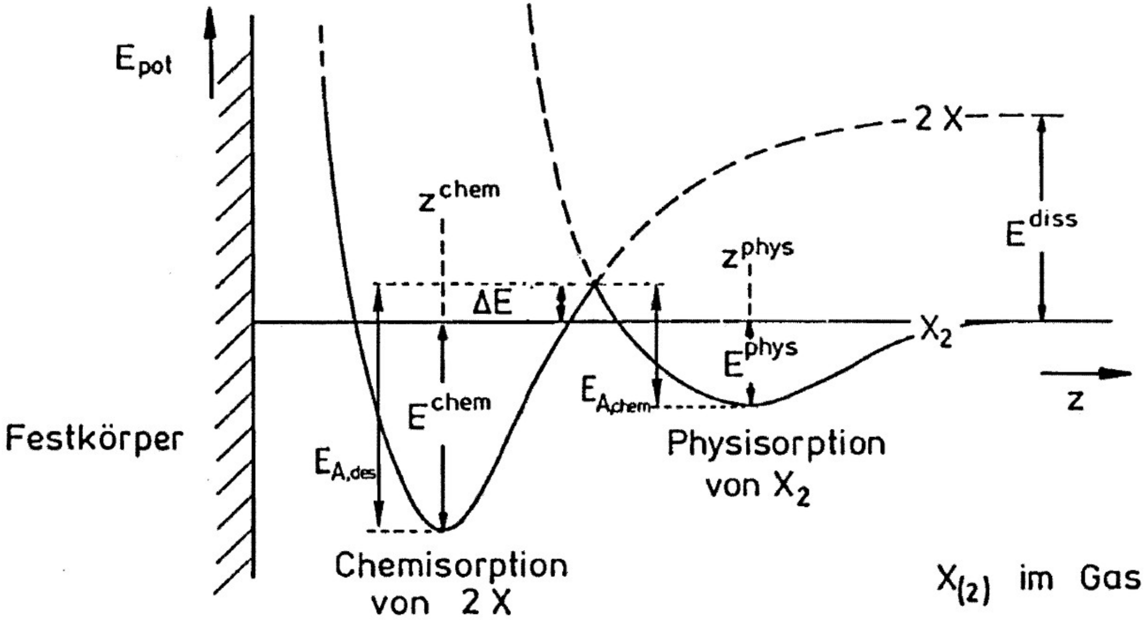
Zangwill: Physics at surfaces, Cambridge

Chemisorption
1) H- terminated Si surface
2) Molecular chemisorption on DB

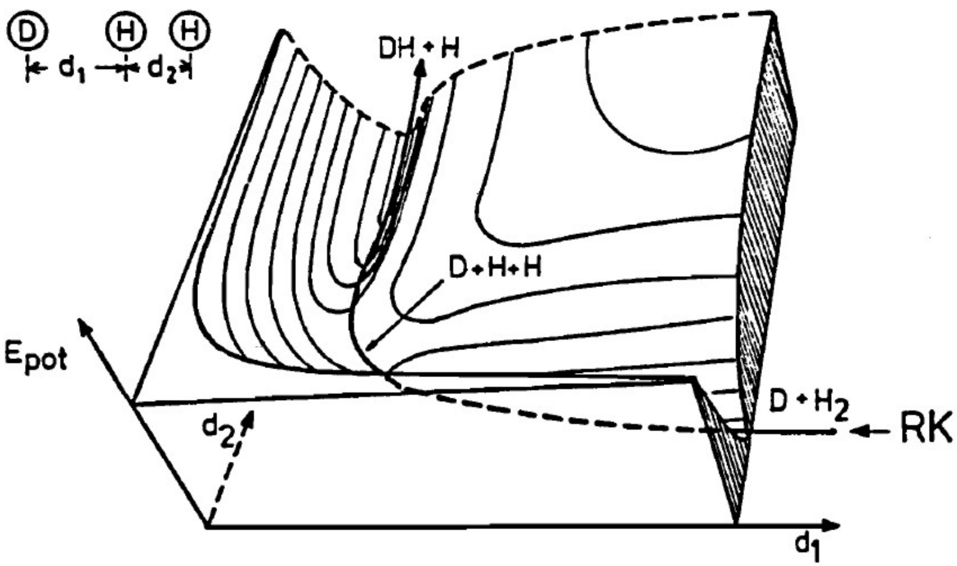


Nature 406, 48 (2000)

Dissociative chemisorption

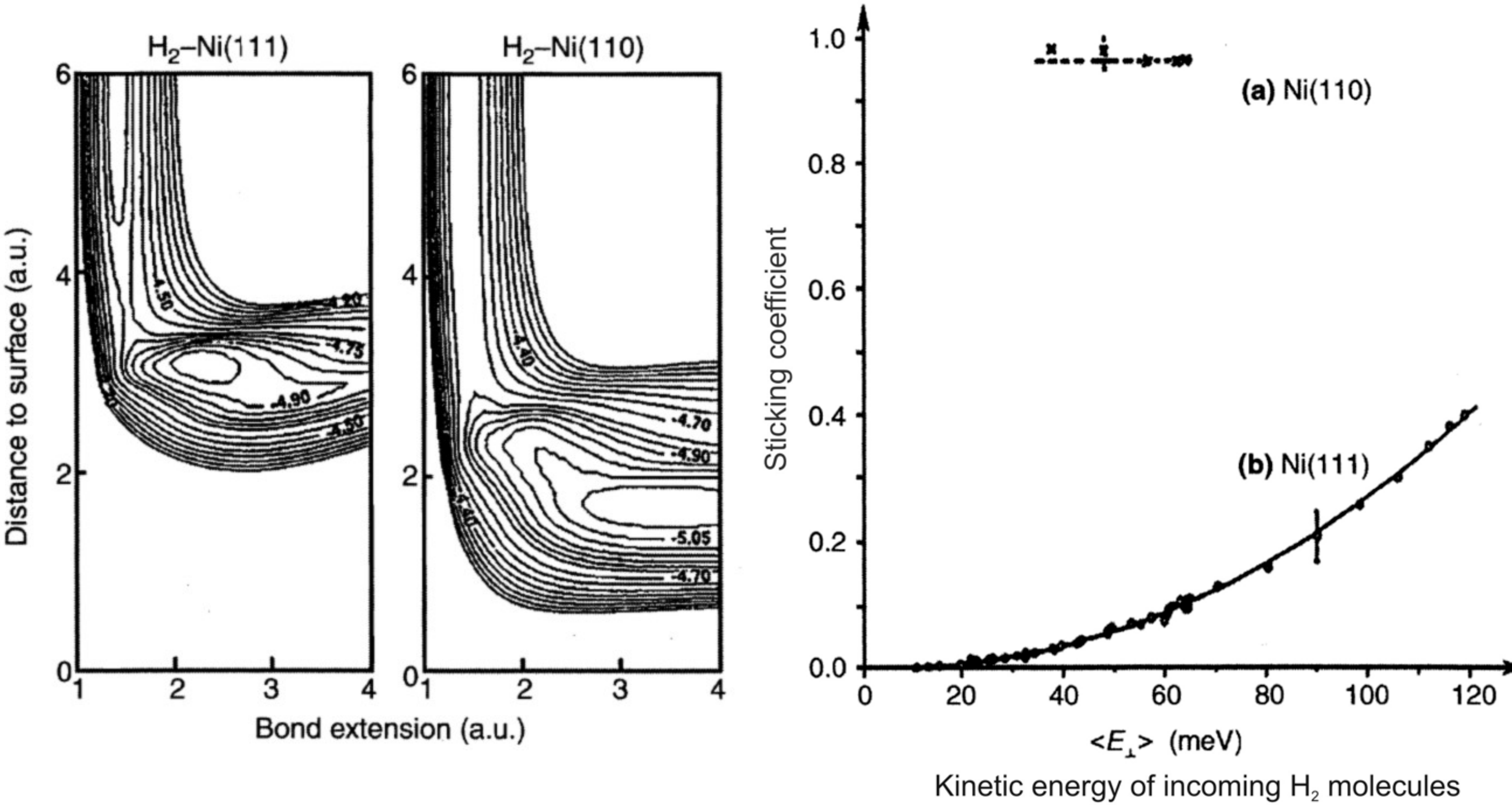


Reaction pathway



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

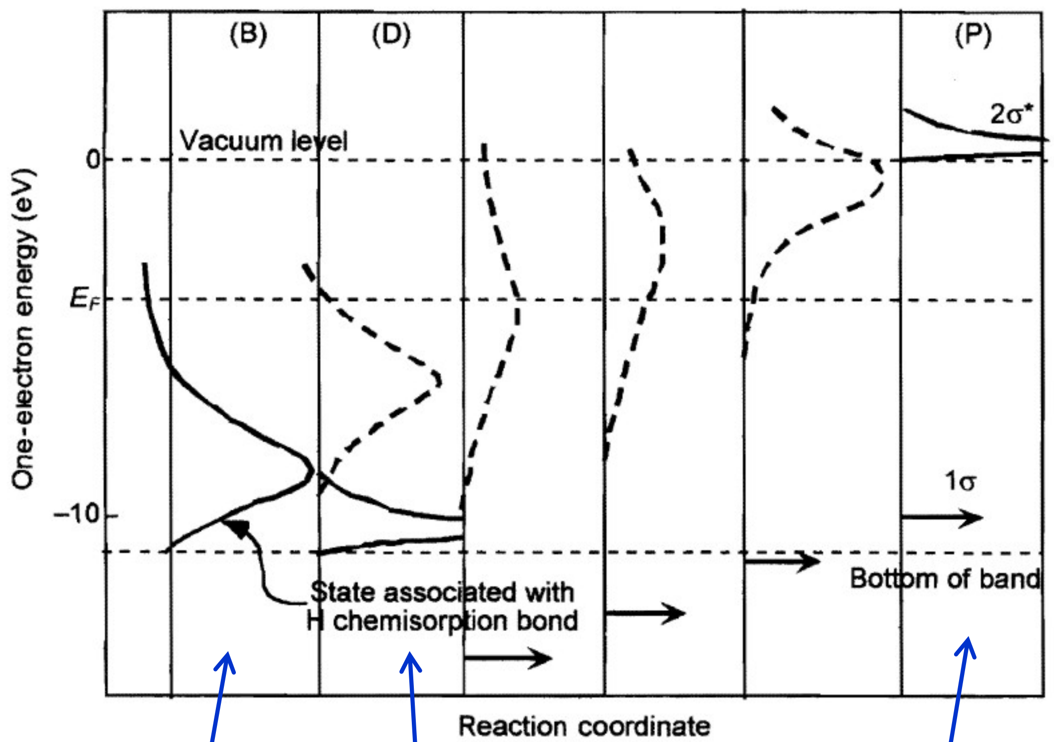
Dissociative chemisorption pathways



G. Ertl: Reactions at Solid Surface, Wiley

Dissociative chemisorption

H_2 approaches Mg surface (calculation)



K. W. Kolasinski: Surface Science, Wiley

Dissociative chemisorption

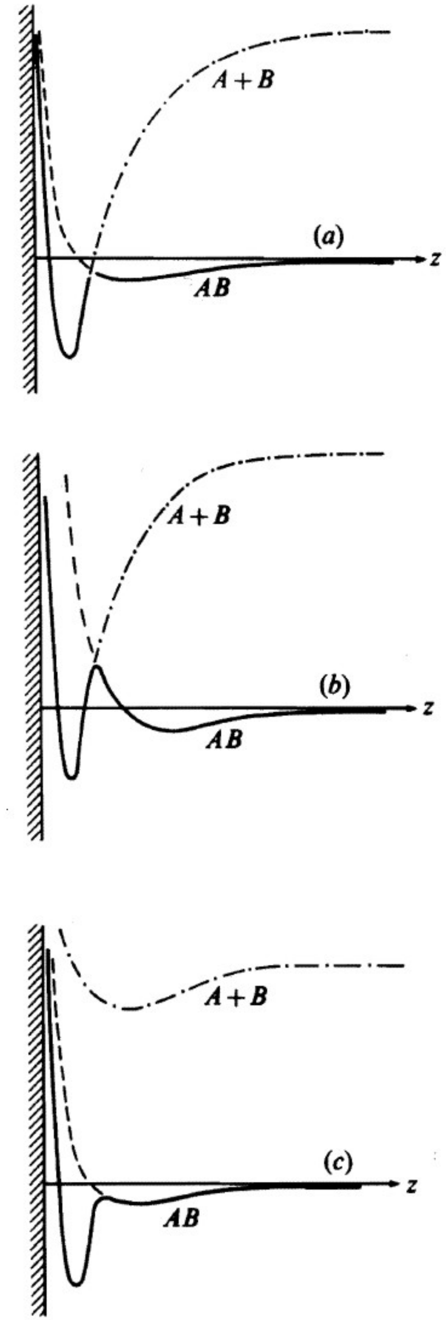
Shortly before dissociation

physisorption

Dissociative chemisorption

Molecular physisorption

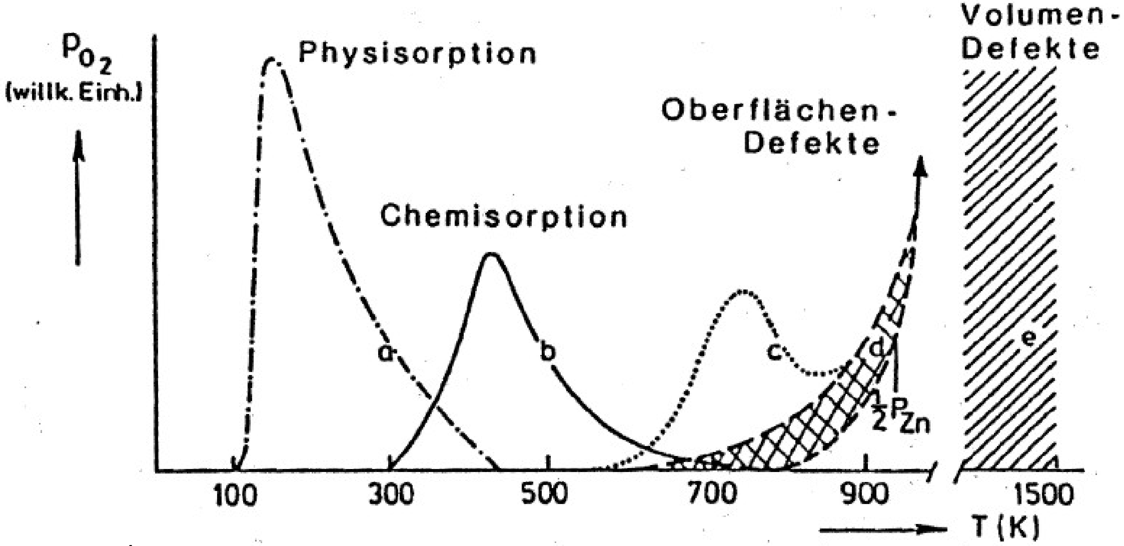
Molecular Chemisorption (non-dissociative)



Zangwill: Physics at surfaces, Cambridge

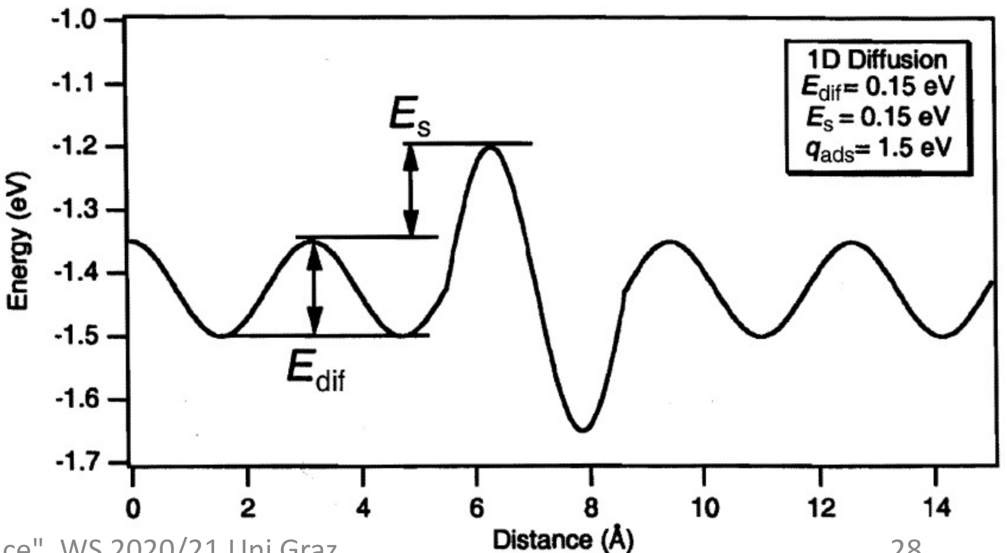
Physisorption vs chemisorption

TDS of O_2/ZnO (with dT/dt = 3.3 Ks^{-1})



Henzler/Göpel:
Oberflächenphysik des Festkörpers
Teubner

Diffusion at a step edge

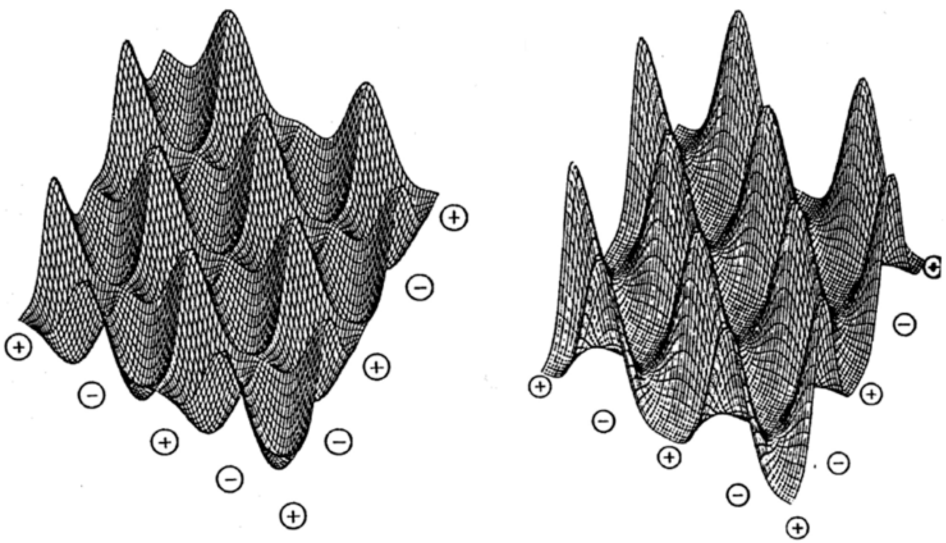


K. W. Kolasinski:
Surface Science
Wiley

Diffusion

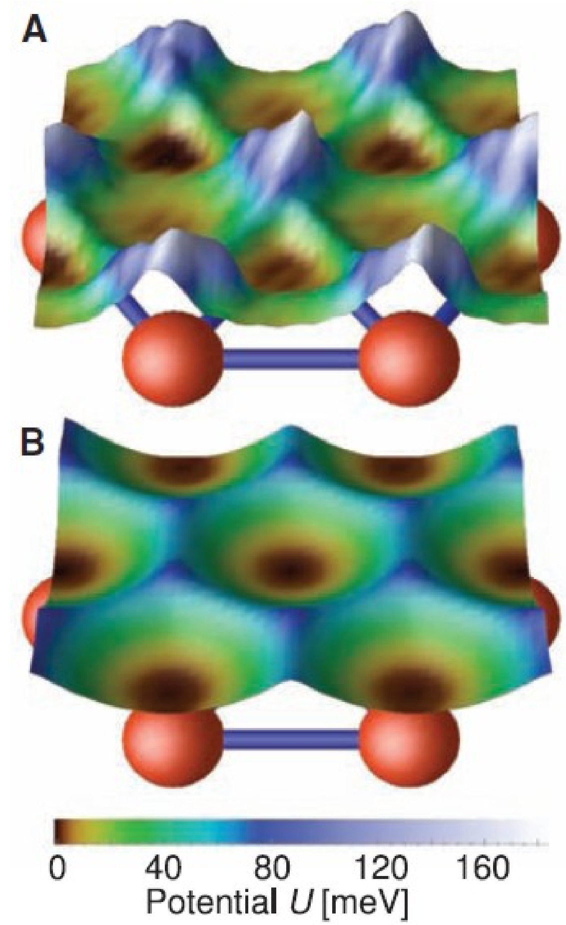
Co (A) and CO (B) on Cu(111)
(AFM force measurements)
Different diffusion barrier over
fcc, hcp and on-top sites

CO_2 on NaCl(100)



CO_2 parallel to the surface *CO_2 perpendicular to the surface*

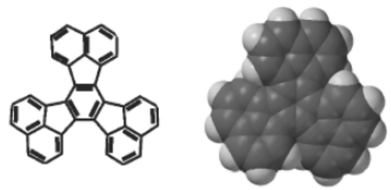
Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner



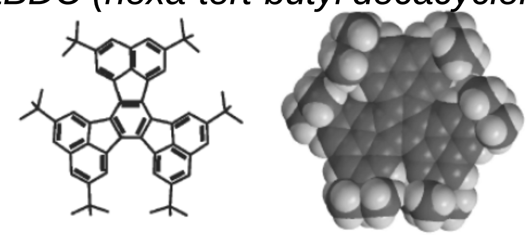
Science 319, 1066 (2008)

Diffusion of molecules

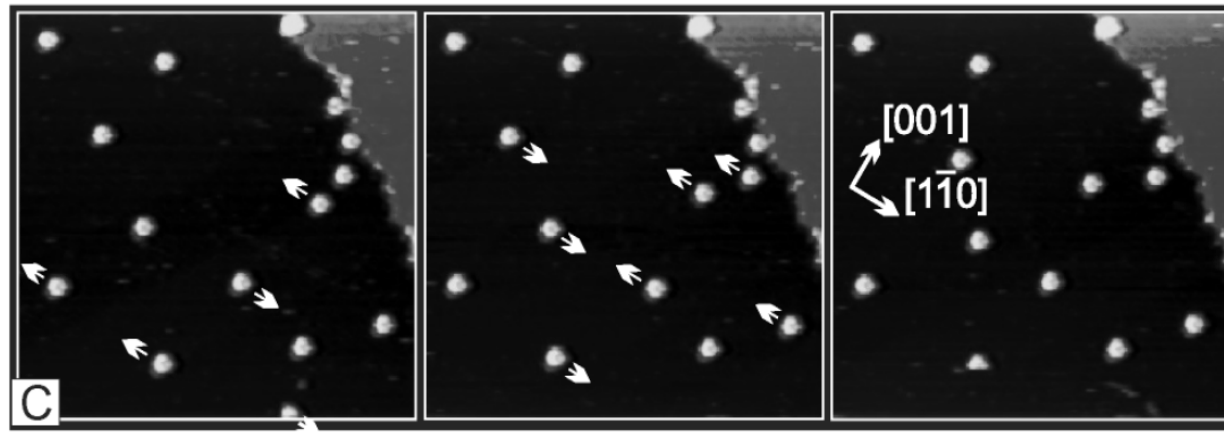
DC (decacyclene)



HtBDC (hexa-tert-butyl decacyclene)



HtBDC on Cu(110) at T = 194 K



M. Schunack et al., Phys. Rev. Lett. 88, 156102 (2002)

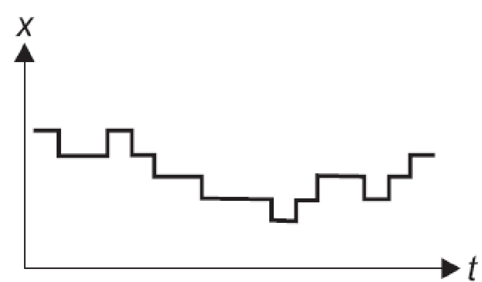
Determination of physical properties:

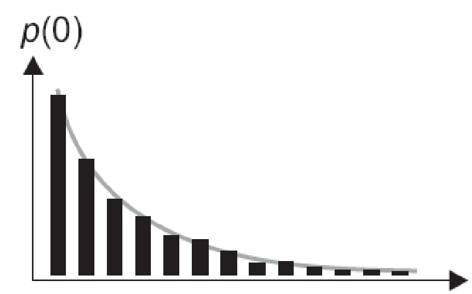
Hopping follows a Poisson distribution
(random events, independent from each other)

→ time intervals between events are
exponentially distributed:

$$p(0) = e^{-ht}$$

p(0): Probability of no jump to occur in time interval t
h: hopping rate



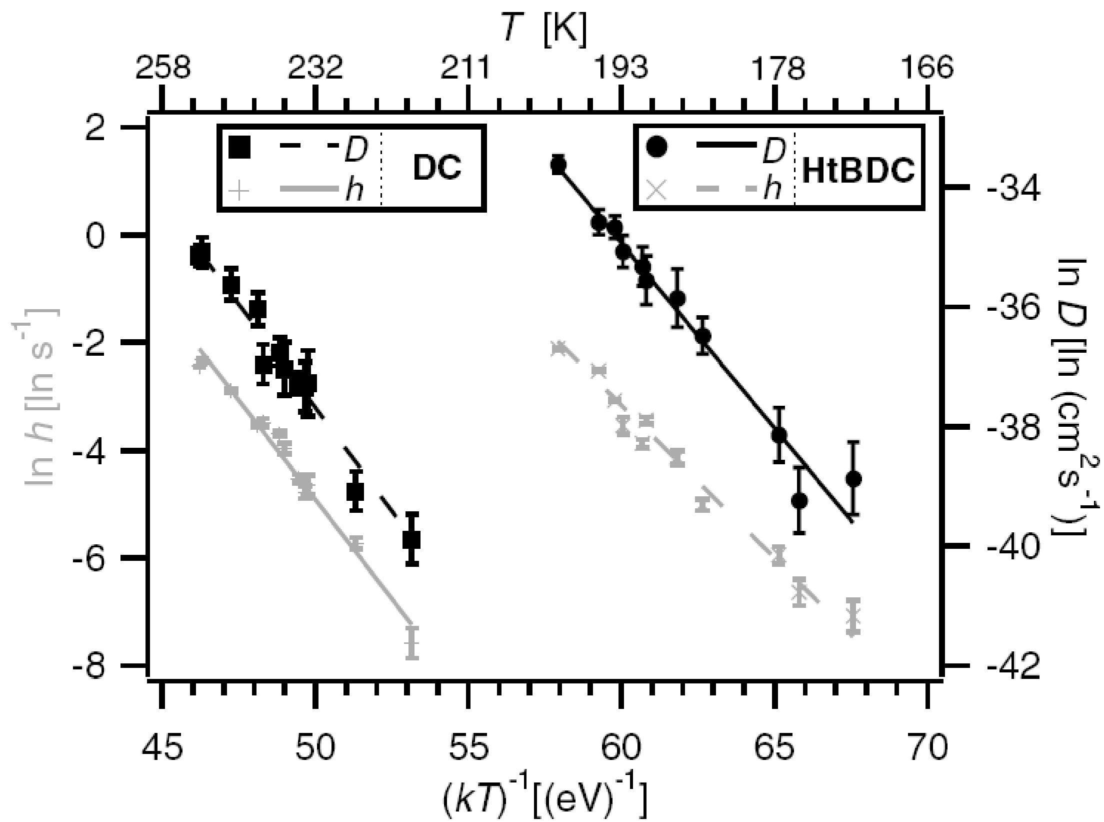


M. Schunack, PhD thesis,
University of Aarhus (2002)

Thus, h can be determined from a residence time distribution if:
- all displacements are considered
- no tip-induced events (i.e. manipulation)
- no multiple displacements occur

Diffusion of molecules

$$h = h_o \cdot e^{\frac{-E_D}{kT}}$$



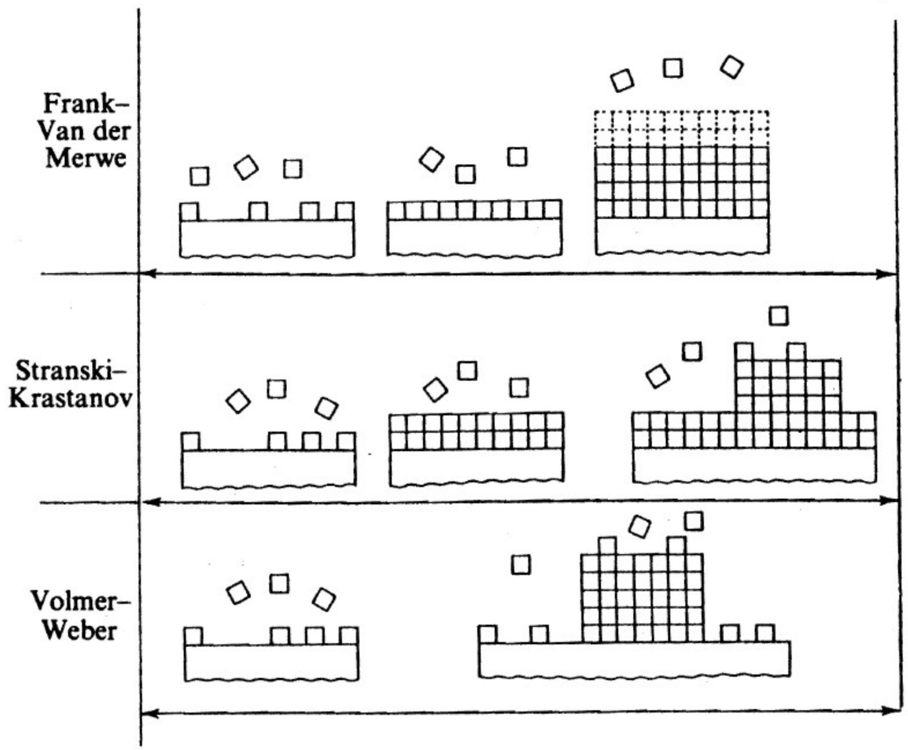
Phys. Rev. Lett. 88, 156102 (2002)

h_o: hopping rate prefactor

E_D: Diffusion barrier

	DC	HtBDC
E_D	0.74 ± 0.03 eV	0.57 ± 0.02 eV

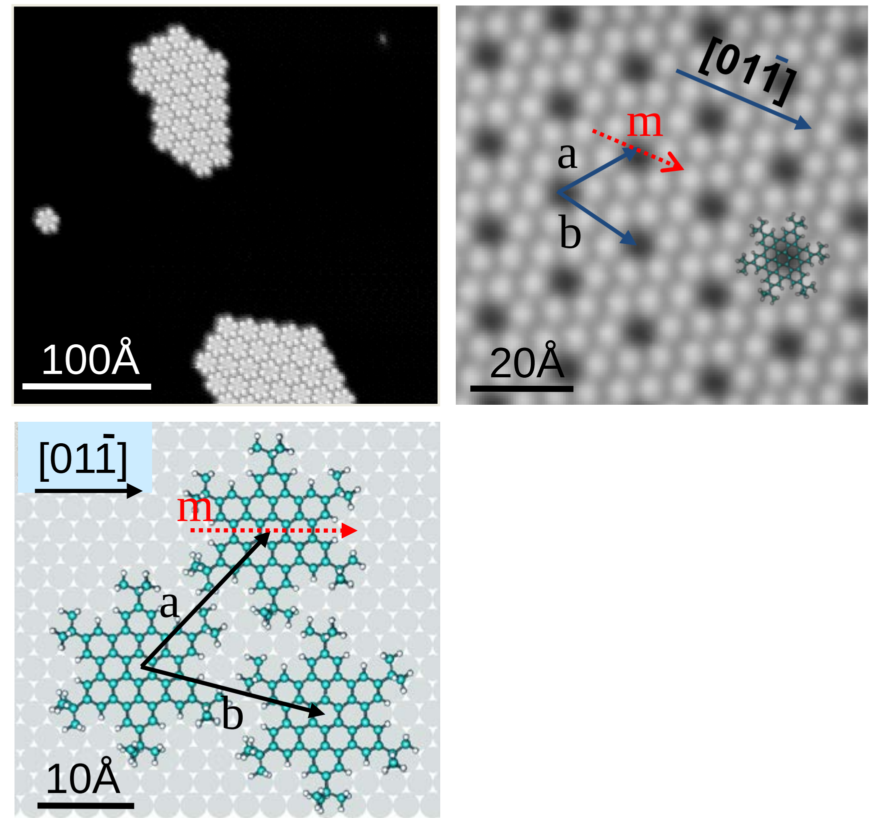
Thin film growth



Zangwill: Physics at surfaces, Cambridge

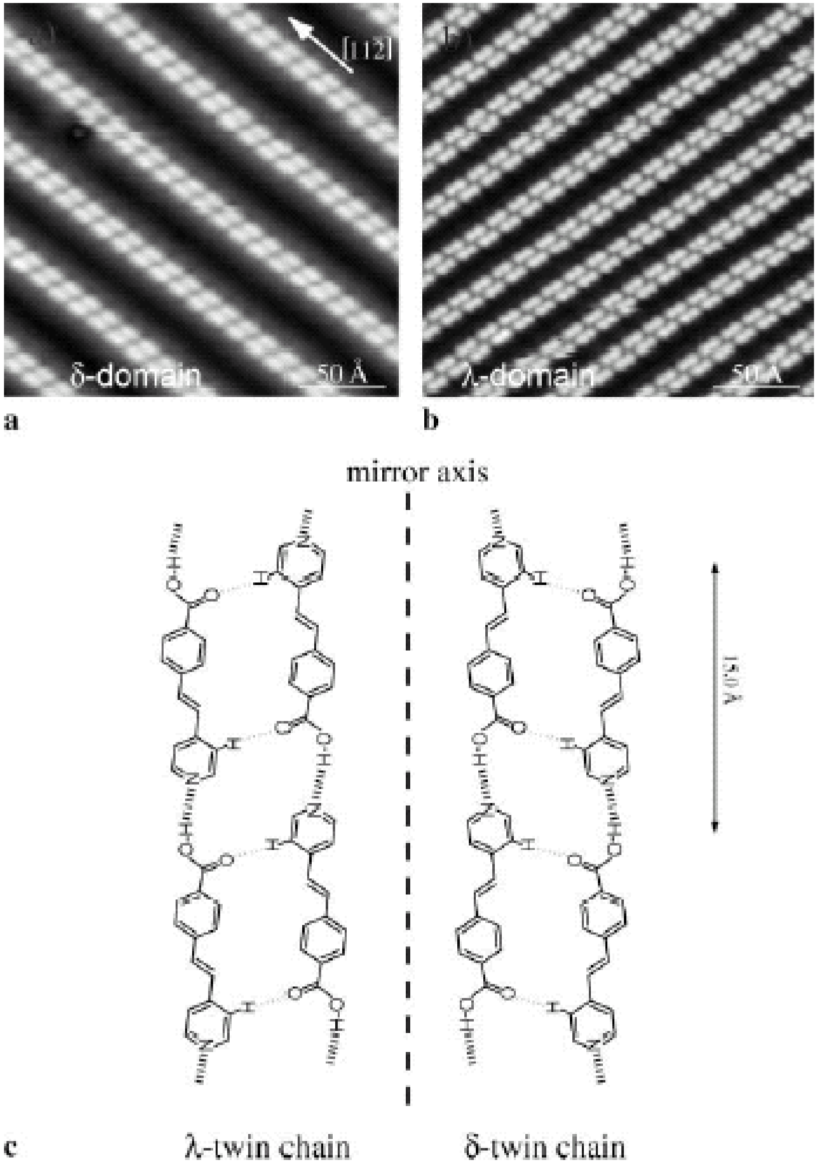
Close-packed molecular structure

HB-HBC on Cu(111)



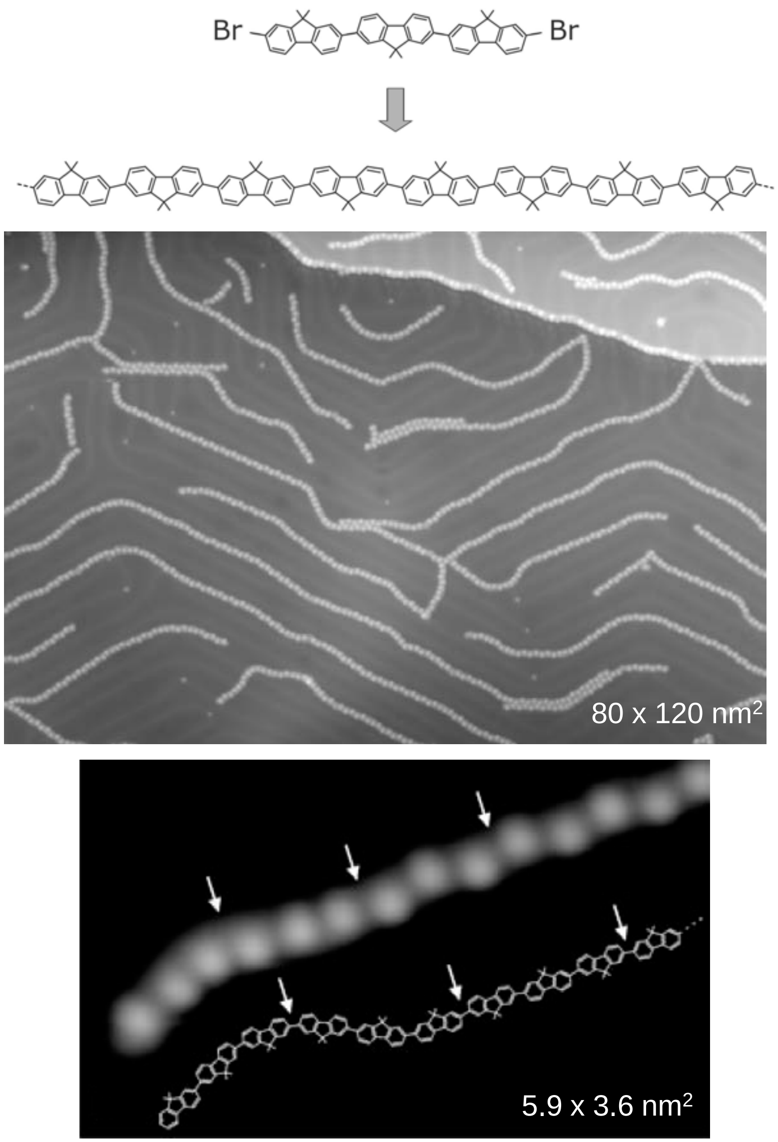
Phys. Rev. B 71, 165428 (2005)

Molecular assembly by H-bonds
PVBA on Ag(111)



Appl. Phys. A 76, 645 (2003)

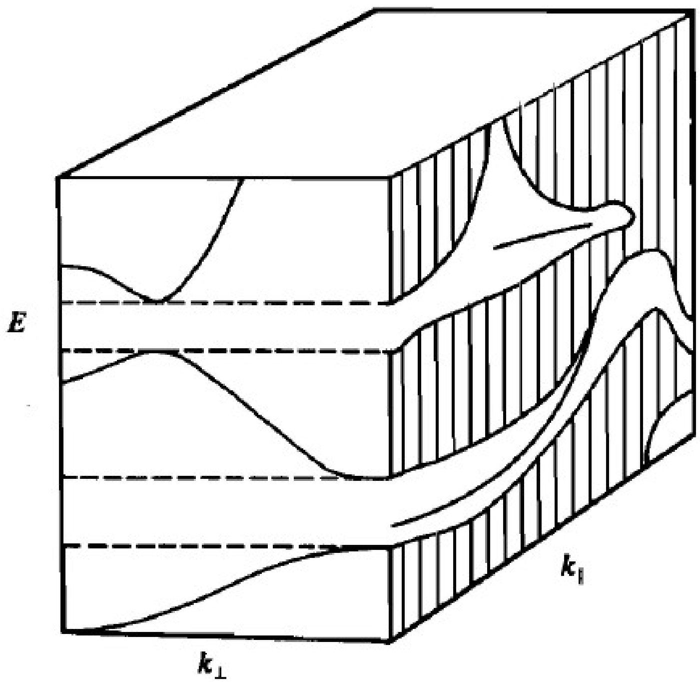
Molecular assembly by covalent bond
DBTF on Au(111)



Science 323, 1193 (2009)

3) Electronic structure of the surface

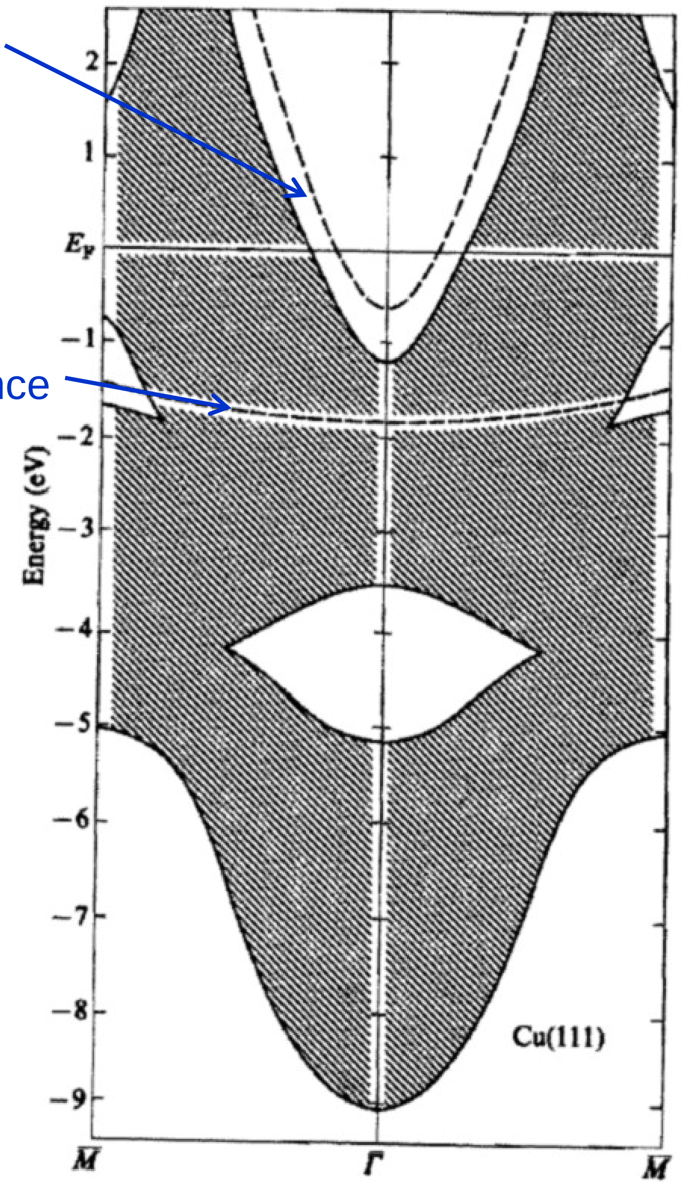
Projected band structure



Zangwill: Physics at Surfaces, Cambridge

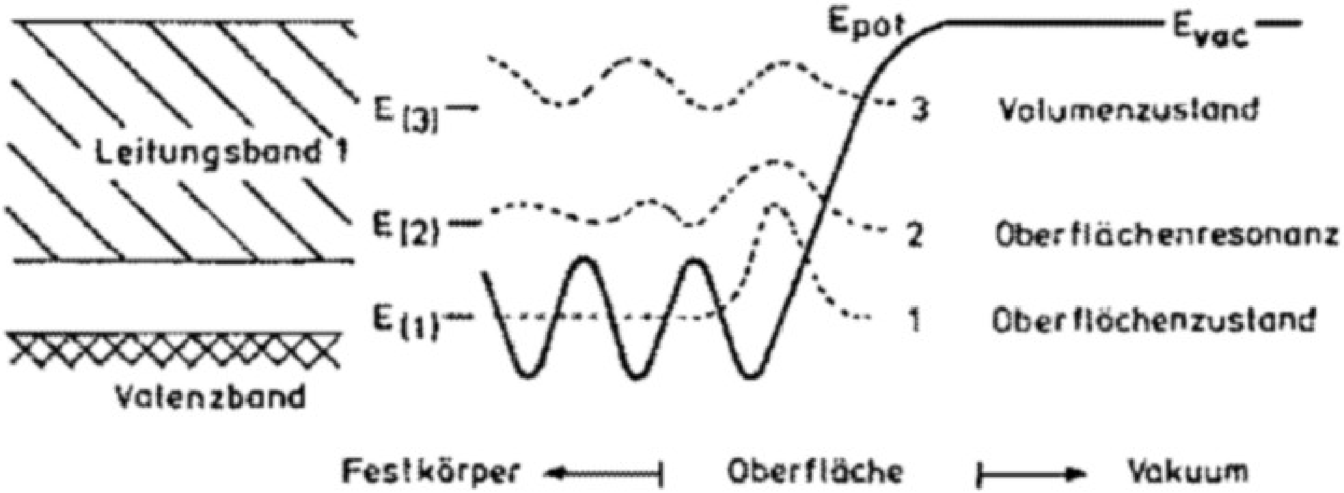
Surface State

Surface Resonance

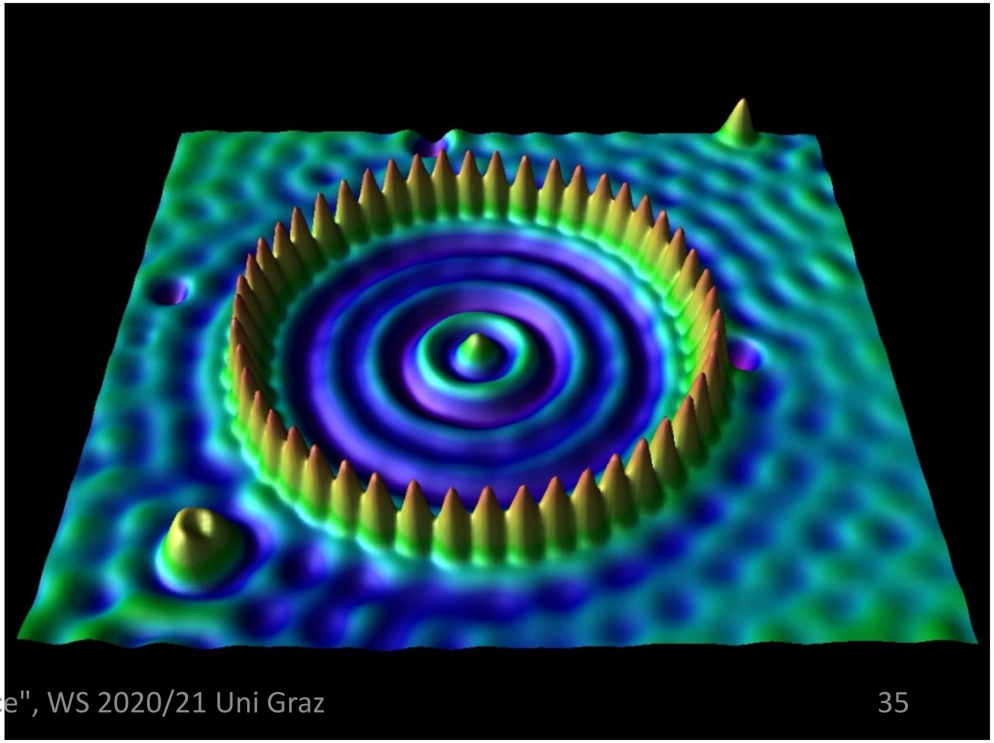


Zangwill: Physics at Surfaces, Cambridge

Probability density



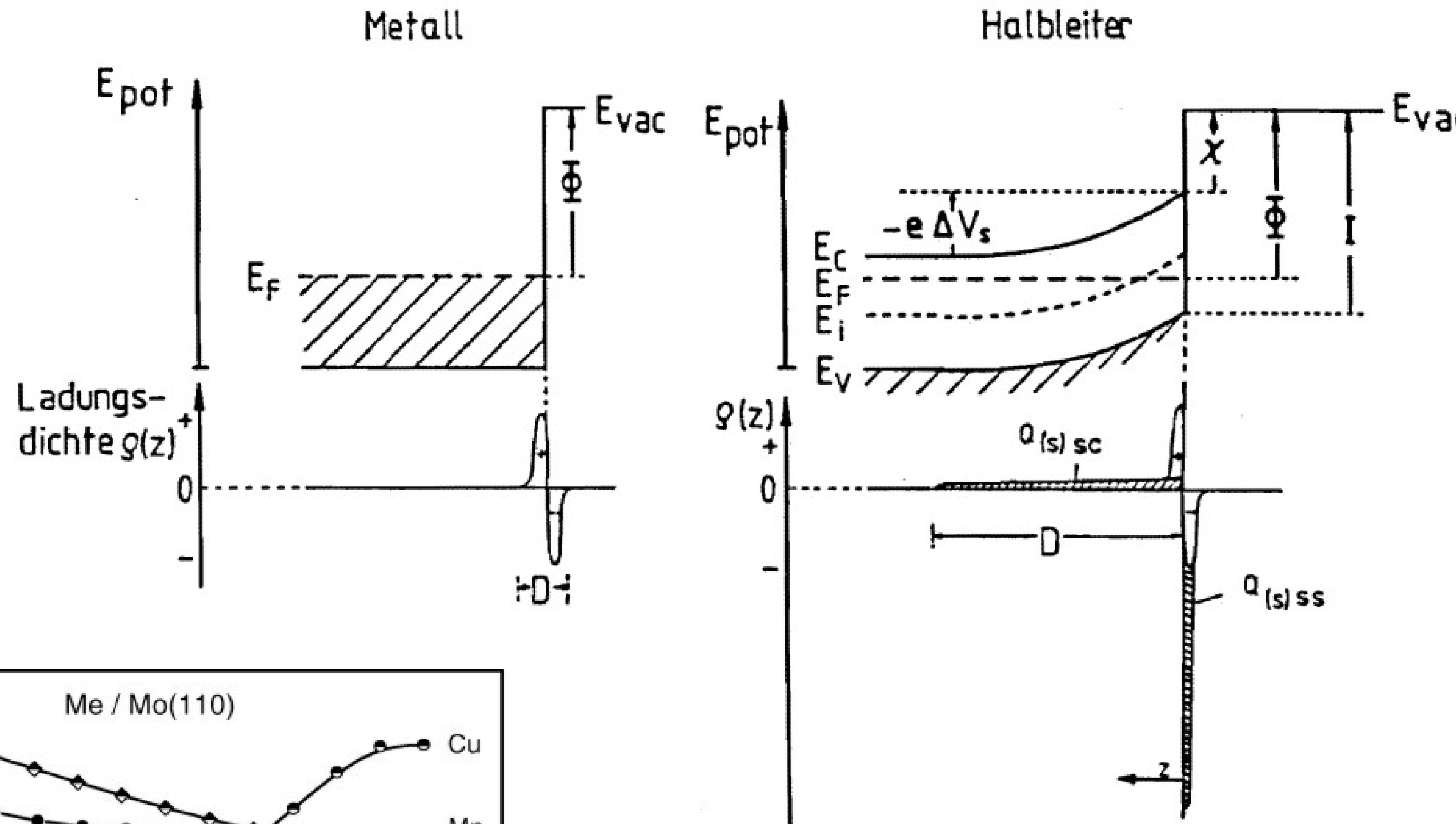
Henzler/Göpel: Oberflächenphysik des Festkörpers Teubner



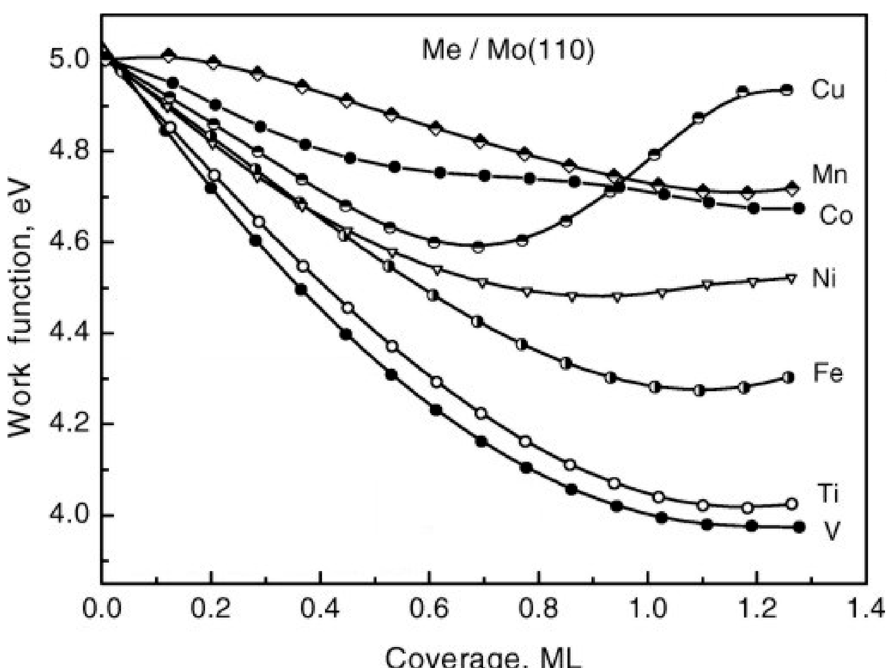
Fe atoms on Cu(111)

D. Eigler et al., Science 262, 218 (1993)

Work function

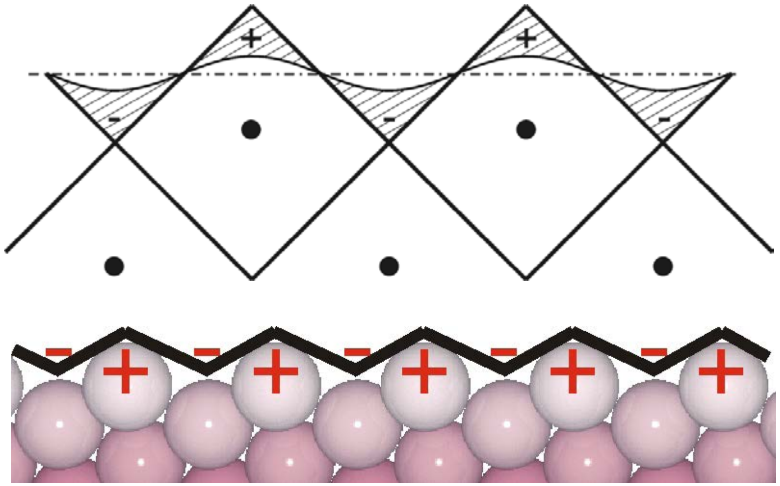


Henzler/Göpel:
Oberflächenphysik des Festkörpers
Teubner



T. T. Magkoev et al.,
J. Phys.: Cond. Matt. 14, L273 (2002)

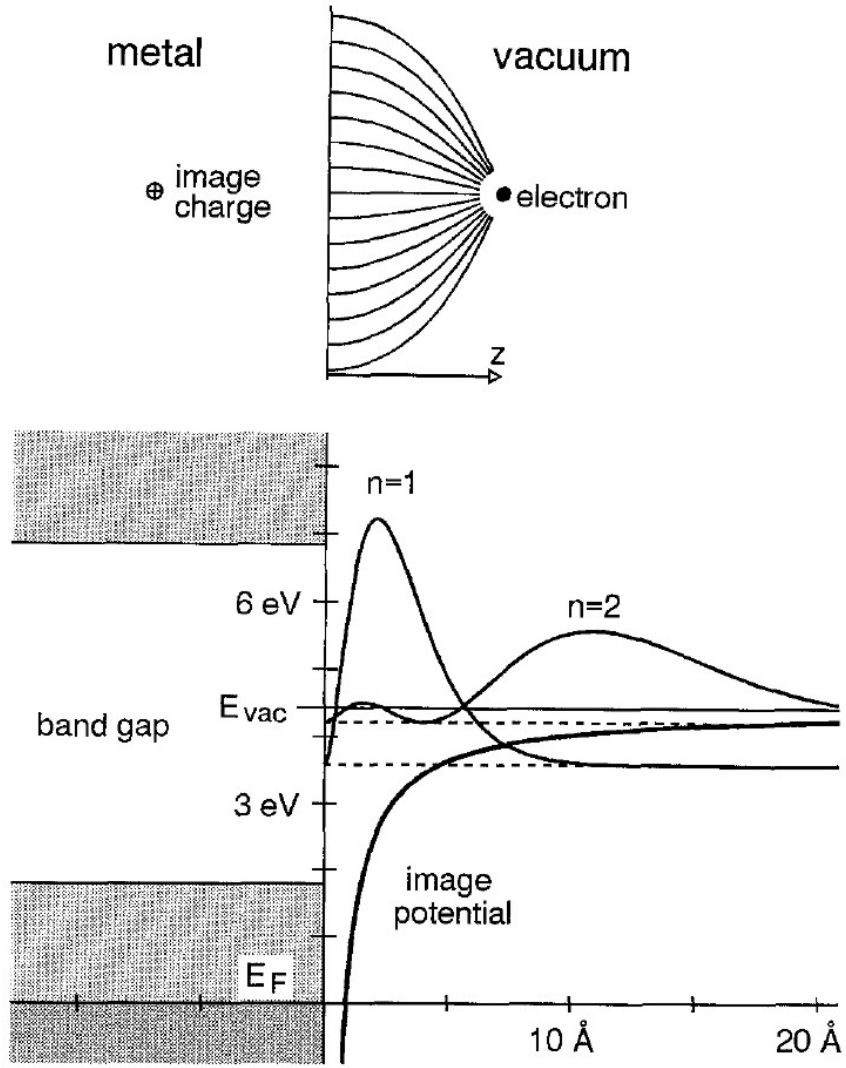
Smoluchowski effect



Dissertation, A. Riemann, FU Berlin 2002

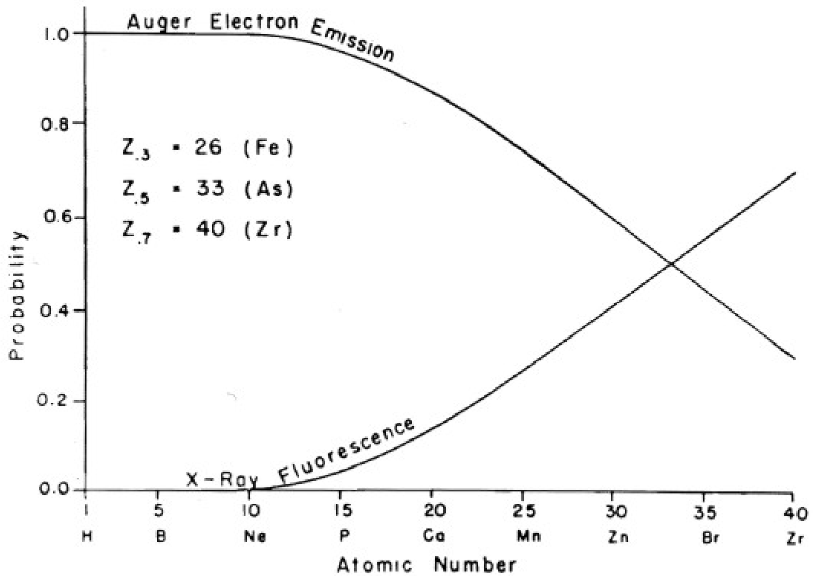
- Charge redistributes on corrugated surfaces
- Work function anisotropy on stepped surfaces

Image potential states



Th. Fauster, Appl. Phys. A 59, 479 (1994)

Auger Electron Spectroscopy (AES)



Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)

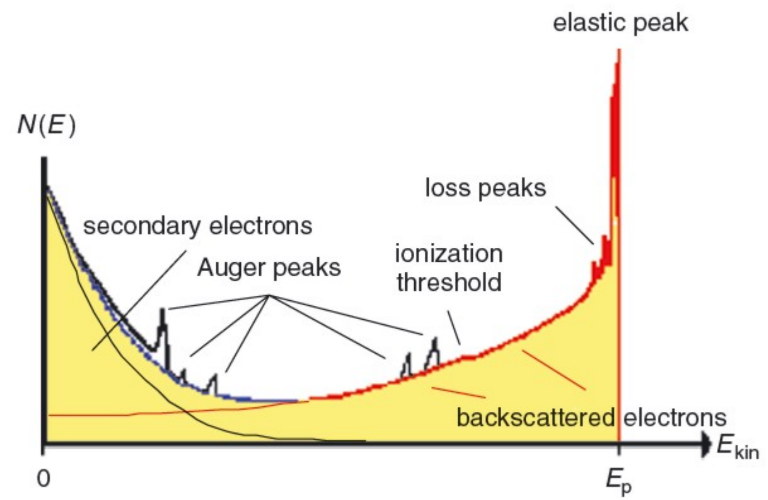


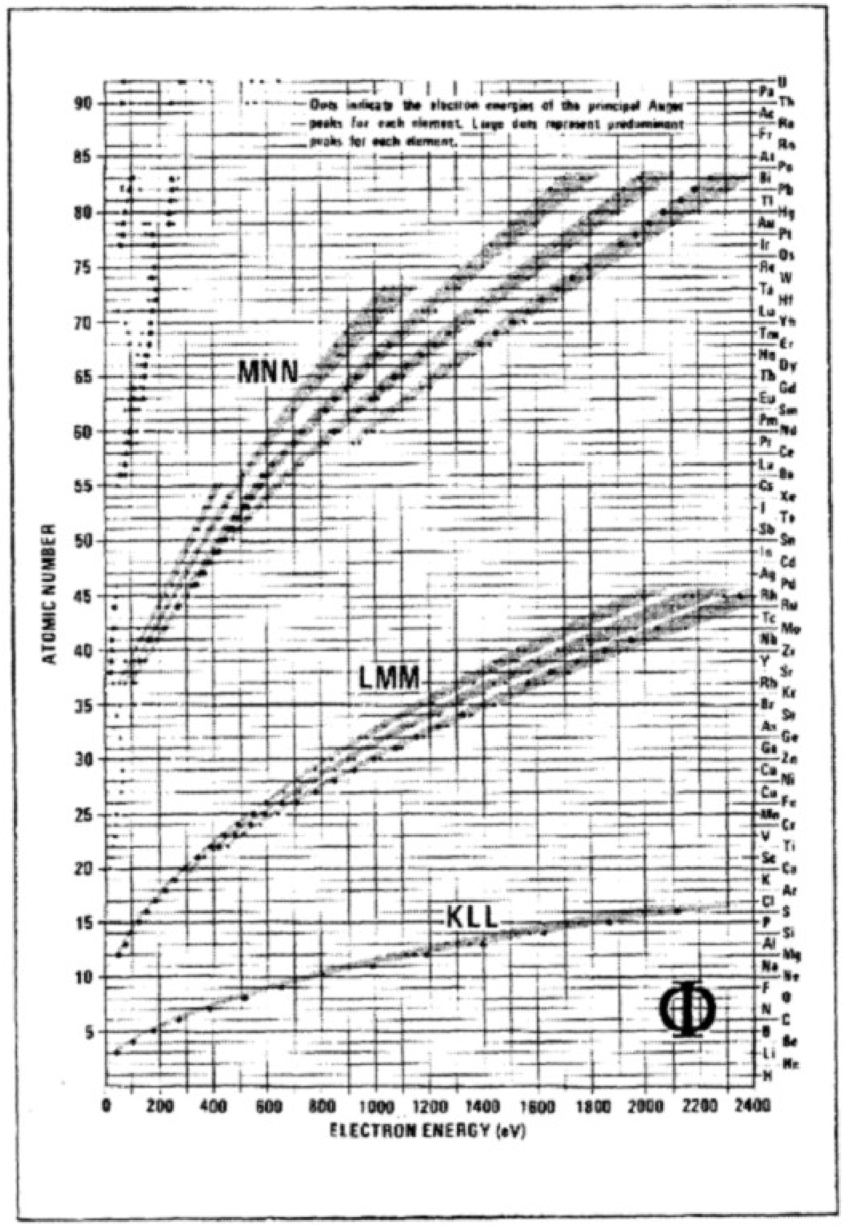
Figure 2.3 Schematic representation of an Auger spectrum

Surface Analysis – The Principal Techniques, Wiley (2009)

AES

Quantum numbers			X-ray suffix	X-ray level	Spectroscopic level
n	l	j			
1	0	$\frac{1}{2}$	1	K	$1s_{1/2}$
2	0	$\frac{1}{2}$	1	L_1	$2s_{1/2}$
2	1	$\frac{1}{2}$	2	L_2	$2p_{1/2}$
2	1	$\frac{3}{2}$	3	L_3	$2p_{3/2}$
3	0	$\frac{1}{2}$	1	M_1	$3s_{1/2}$
3	1	$\frac{1}{2}$	2	M_2	$3p_{1/2}$
3	1	$\frac{3}{2}$	3	M_3	$3p_{3/2}$
3	2	$\frac{3}{2}$	4	M_4	$3d_{3/2}$
3	2	$\frac{5}{2}$	5	M_5	$3d_{5/2}$
	etc.		etc.	etc.	etc.

Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)



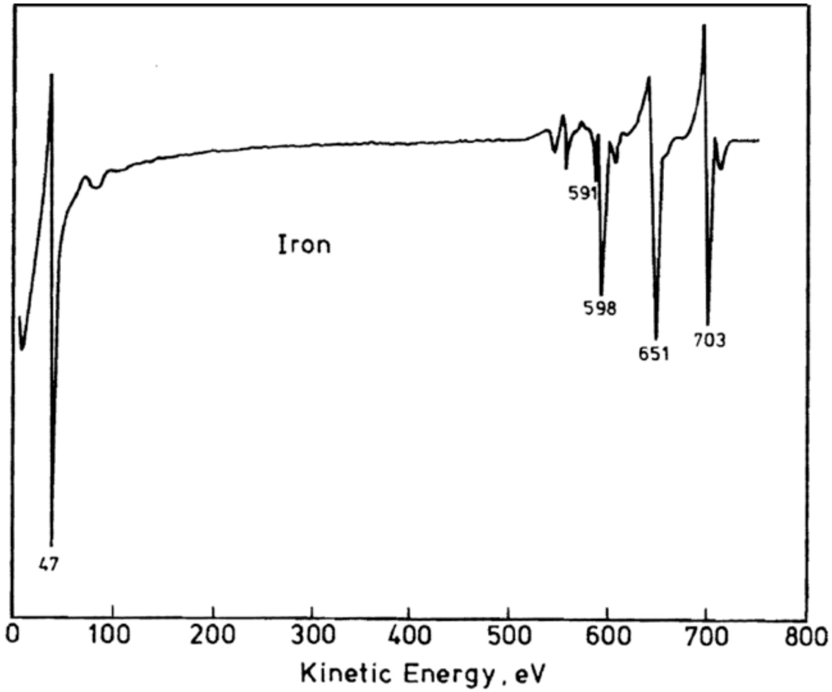
Handbook of Auger Electron Spectroscopy (1978)

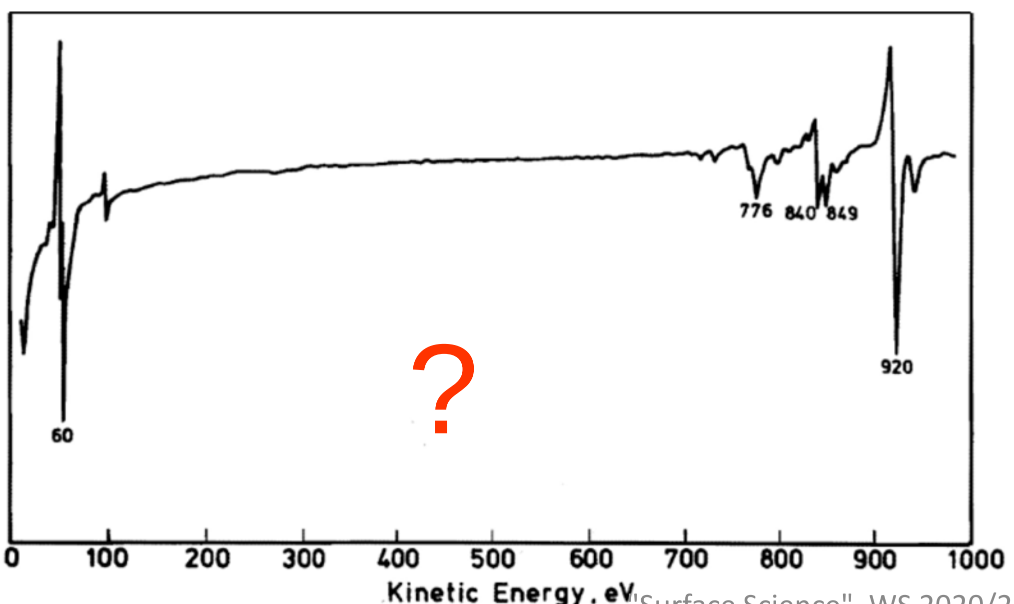
Electron binding energies (in eV)

Z	EL	K	L1	L2	L3	M1	M2	M3	M4	M5
1	H	13.6								
2	HE	24.6								
3	LI	54.8	5.3							
4	BE	112.1	8.0							
5	B	188.0	12.6	4.7	4.7					
6	C	283.8	18.0	6.4	6.4					
7	N	401.6	24.4	9.2	9.2					
8	O	532.0	28.5	7.1	7.1					
9	F	685.4	34.0	8.6	8.6					
10	NE	870.1	48.5	21.7	21.6					
11	NA	1072.1	63.3	31.1	31.1	0.7				
12	MG	1305.0	89.4	51.4	51.4	2.1				
13	AL	1559.6	117.7	73.2	72.7	0.7	5.5	5.5		
14	SI	1838.9	148.7	99.5	98.9	7.6	3.0	3.0		
15	P	2145.5	189.3	136.2	135.3	16.2	9.9	9.9		
16	S	2472.0	229.2	165.4	164.2	15.8	8.0	8.0		
17	CL	2822.4	270.2	201.6	200.0	17.5	6.8	6.8		
18	AR	3206.0	326.3	250.7	248.6	29.2	15.9	15.8		
19	K	3607.4	377.1	296.3	293.6	33.9	17.8	17.8		
20	CA	4038.1	437.8	350.0	346.4	43.7	25.4	25.4		
21	SC	4492.8	500.4	406.7	402.2	53.8	32.3	32.3	6.6	6.6
22	TI	4966.4	563.7	461.5	455.5	60.3	34.6	34.6	3.7	3.7
23	V	5465.1	628.2	520.5	512.9	66.5	37.8	37.8	2.2	2.2
24	CR	5989.2	694.6	583.7	574.5	74.1	42.5	42.5	2.3	2.3
25	MN	6539.0	769.0	651.4	640.3	83.9	49.6	48.6	3.3	3.3
26	FE	7112.0	846.1	721.1	708.1	92.9	54.0	54.0	3.6	3.6
27	CO	7708.9	925.6	793.6	778.6	100.7	59.5	59.5	2.9	2.9
28	NI	8332.8	1008.1	871.9	854.7	111.0	68.1	68.1	3.6	3.6
29	CU	8978.9	1096.1	951.0	931.1	119.8	73.6	73.6	1.6	1.6
30	ZN	9658.6	1193.6	1042.8	1019.7	135.9	96.6	86.6	8.1	8.1

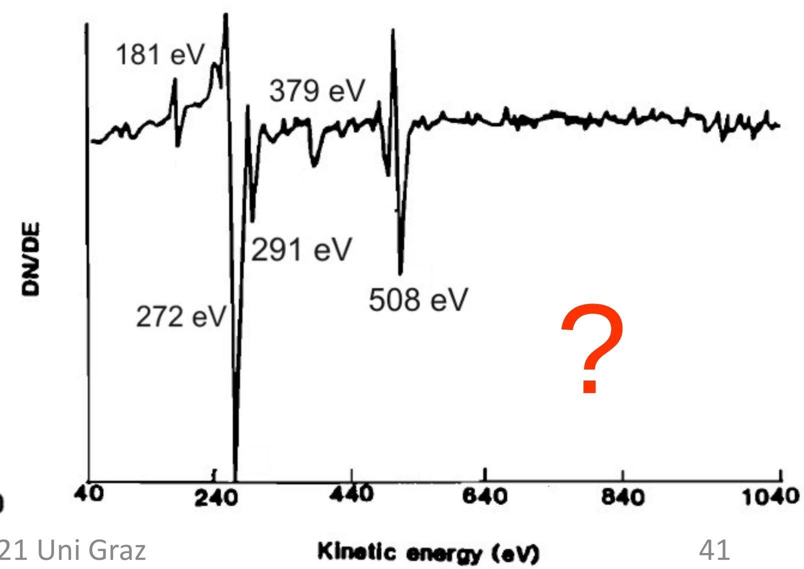
Atom. Data Nucl. Data Tables 20, 311 (1977)

Examples

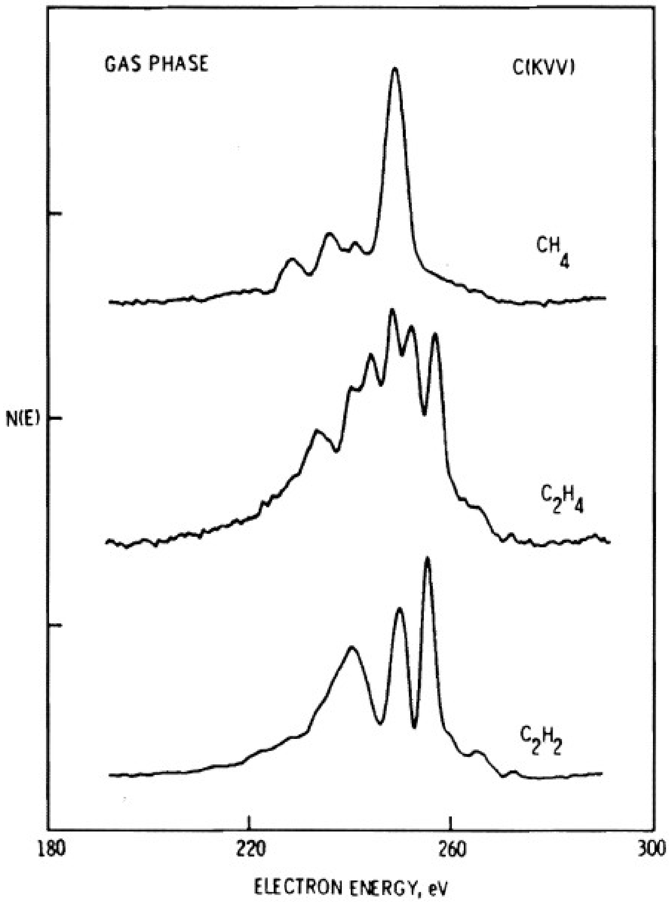




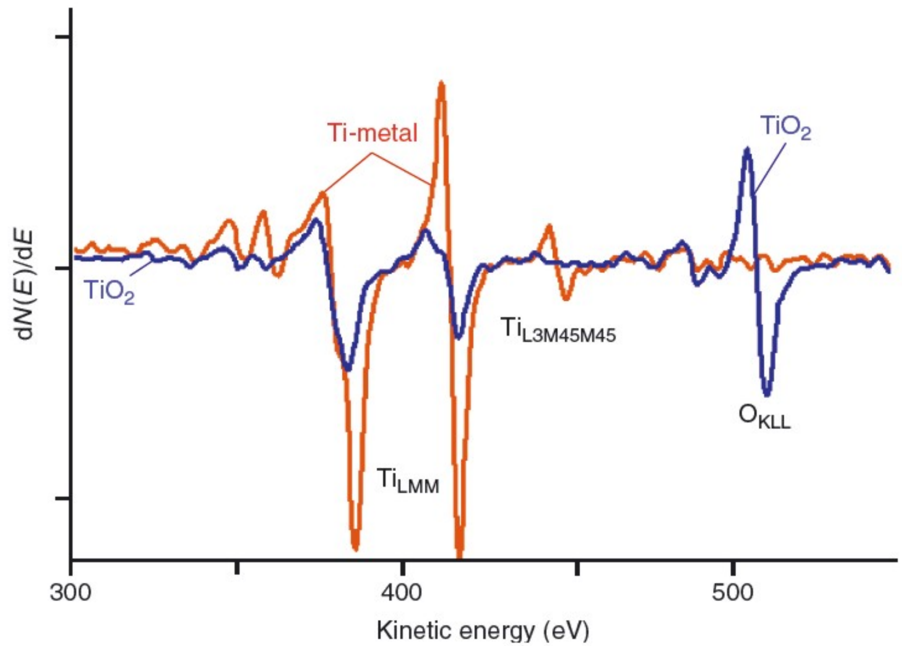
Spittle after drinking Cola



Auger chemical fine structure



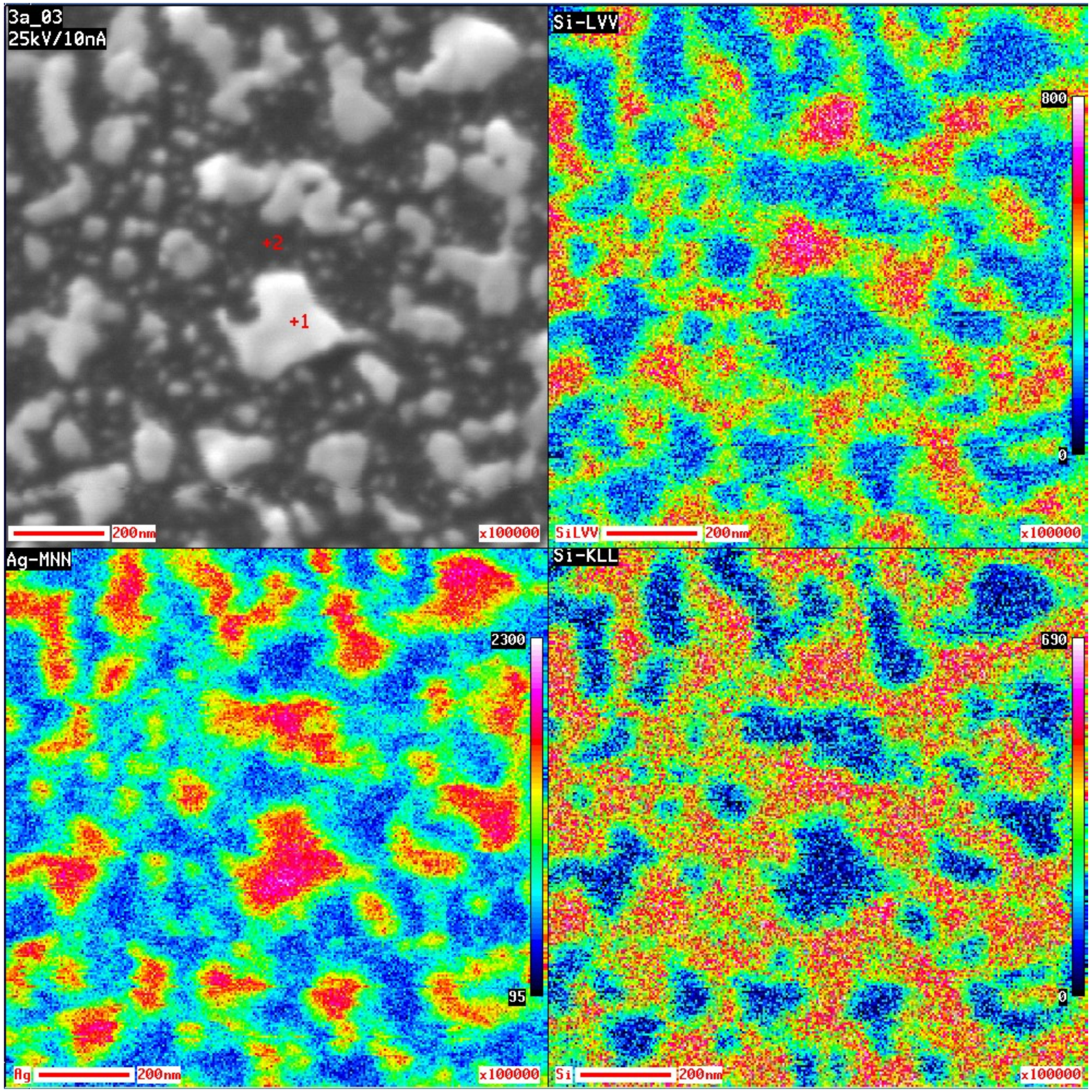
Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)



Surface Analysis – The Principal Techniques, Wiley (2009)

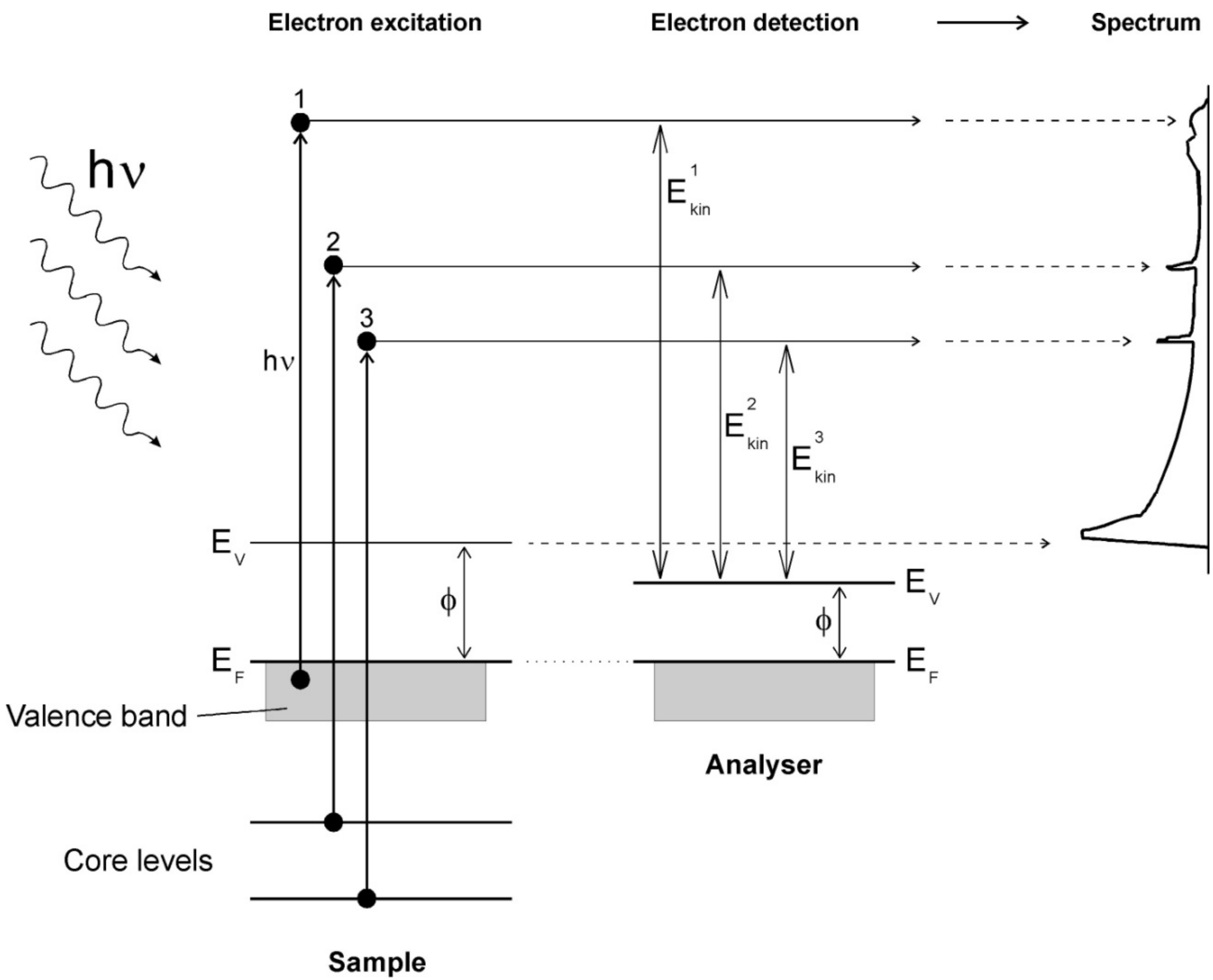
Scanning Auger Microscopy (SAM)

Ag clusters on a Si surface



Alberta Centre for Surface Engineering and Science (ACSES)

Photoelectron spectroscopy



Photoemissionsspektroskopie

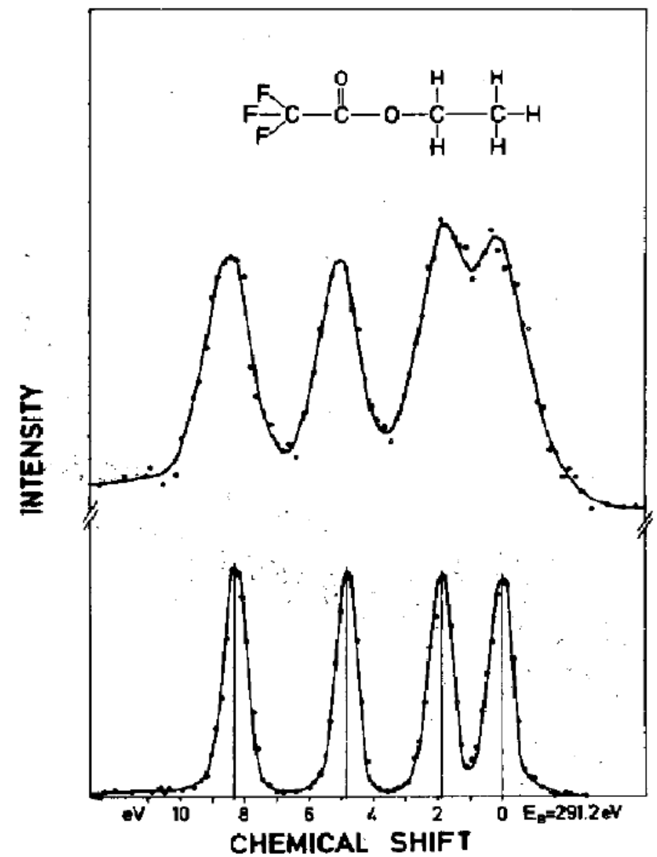
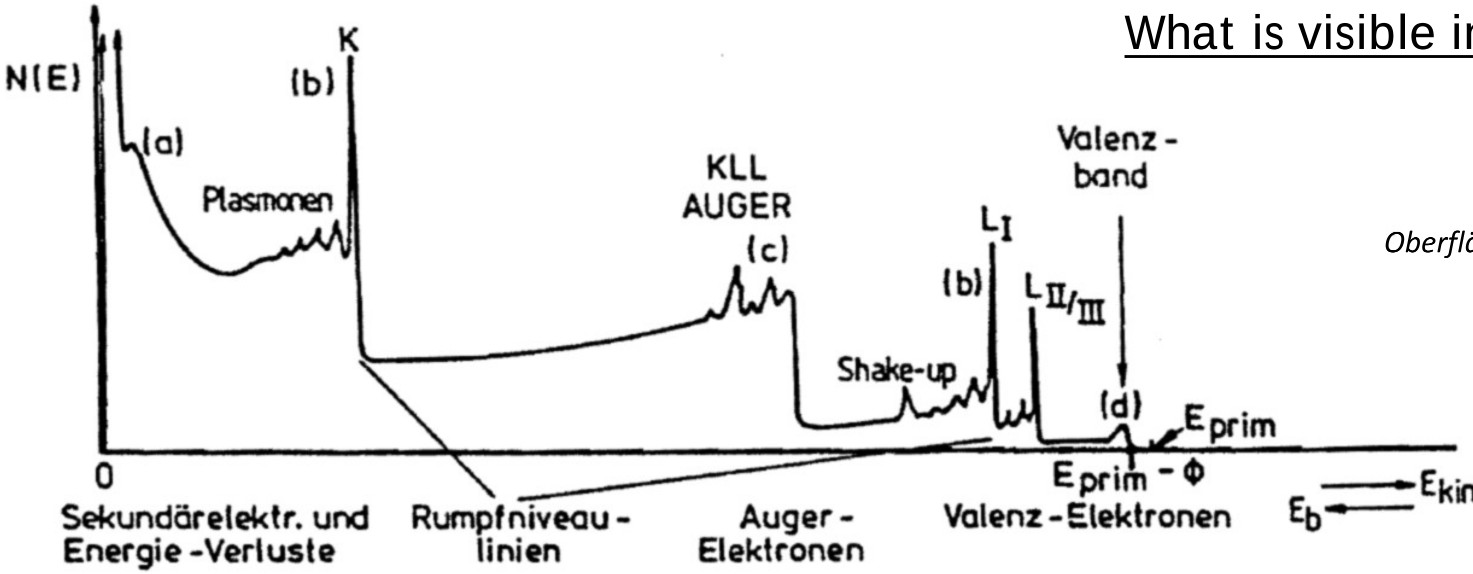


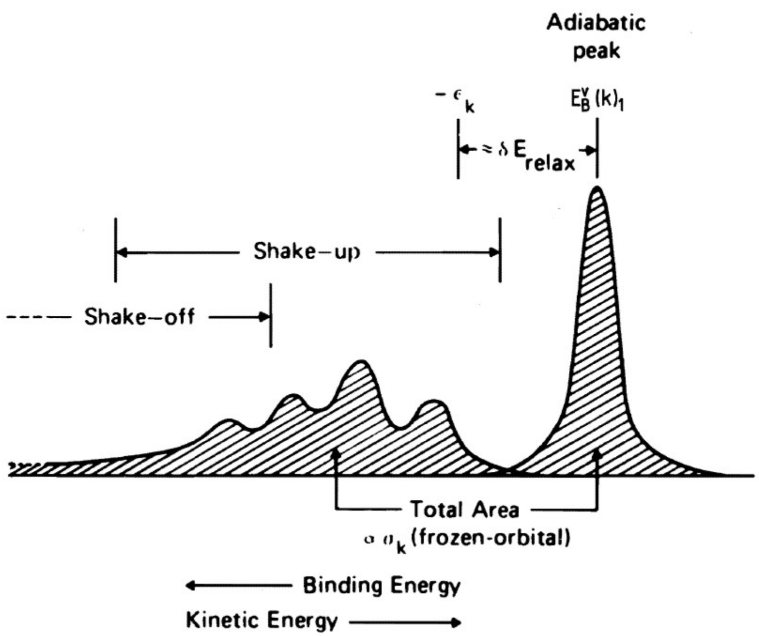
Fig. 28. The ESCA shifts of the C 1s in ethyl trifluoroacetate.
Upper spectrum without and lower with monochromatization.

K. Siegbahn, J. El. Spectr. Rel. Phen. 5, 3 (1974)

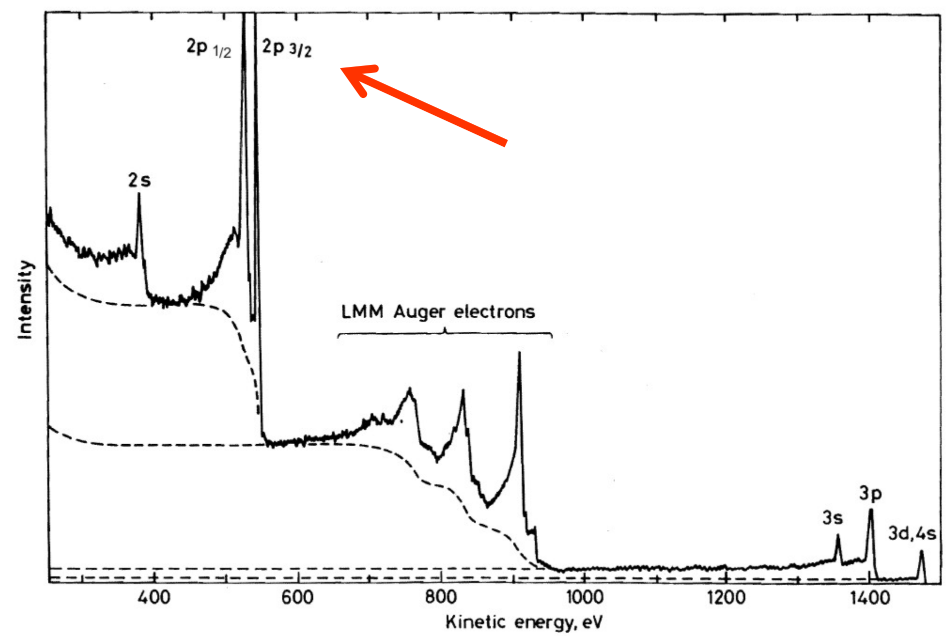
What is visible in a XPS spectrum?



Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner



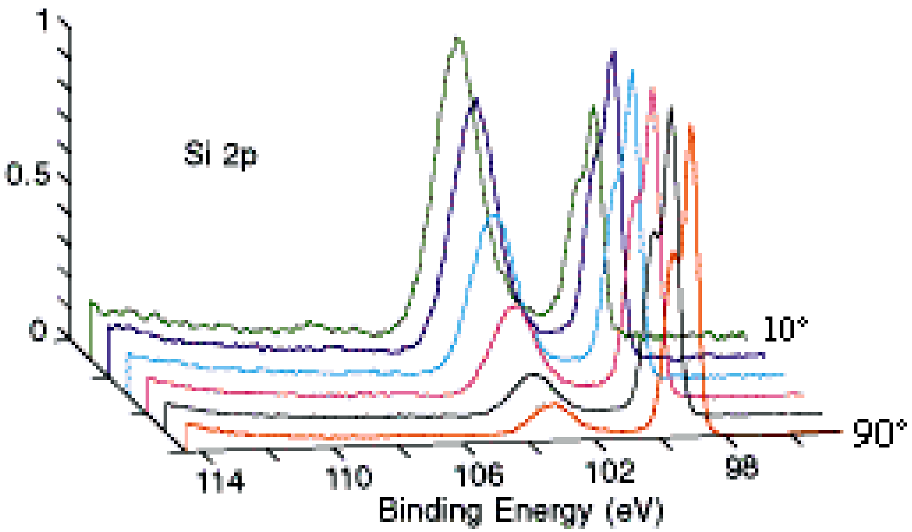
Ertl/Küppers, Low energy electrons and surface chemistry, VCH



Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)

Angle dependence

Si sample covered with an oxide layer
Si 2p for different emission angles

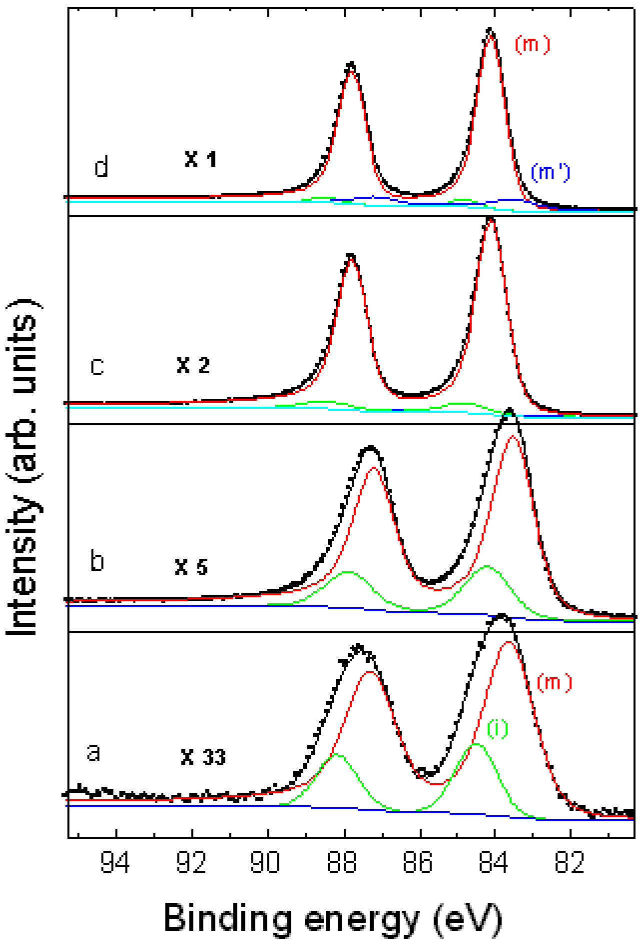


Physical Electronics, Inc. (PHI)

Si peak of the oxide at 103 eV changes…

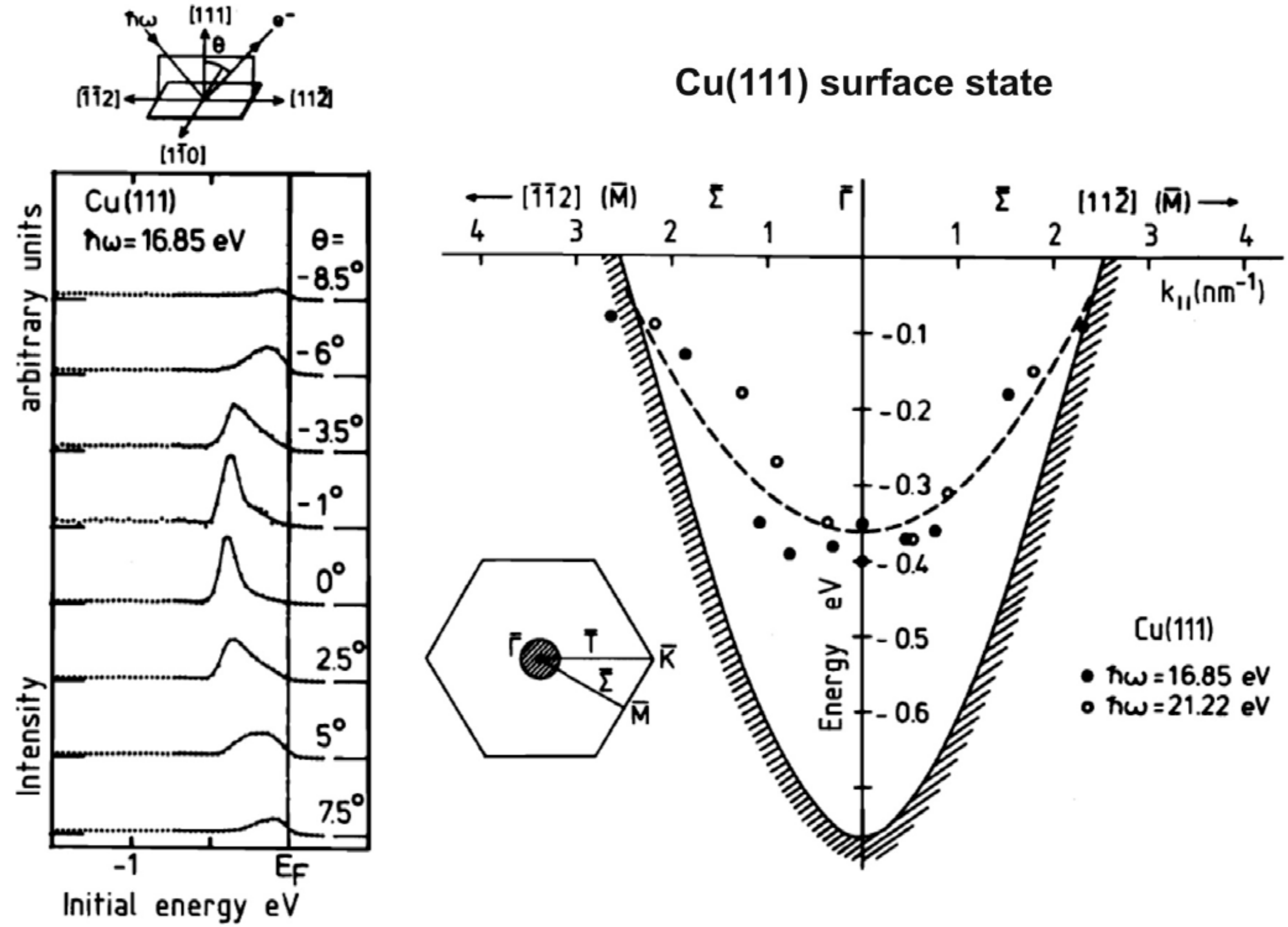
Fitting

Au on GaN (Au 4f peaks)
Increasing Au coverage (from a to d)



R. Sporken et al.

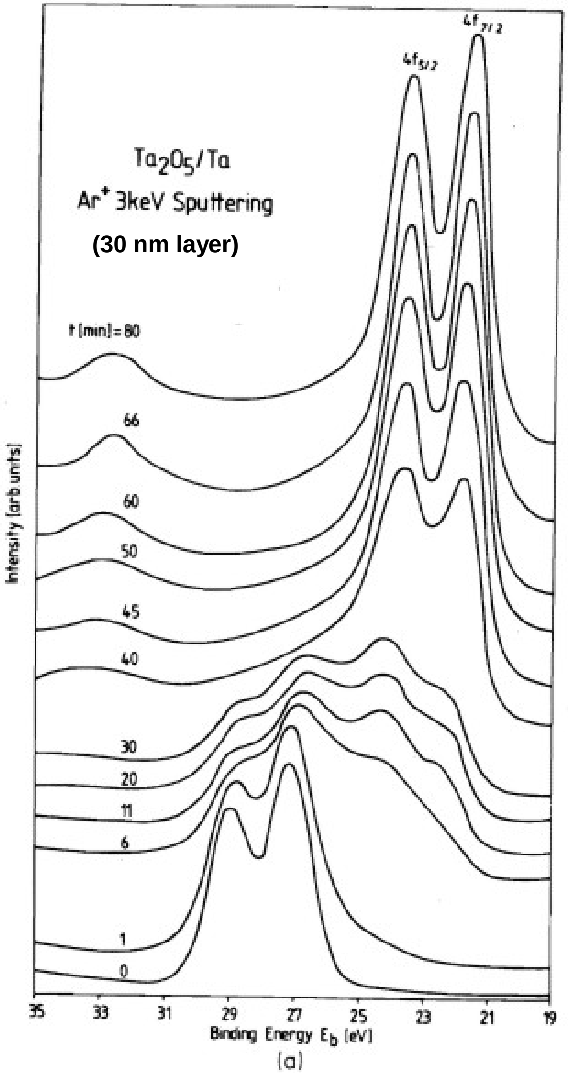
Angle resolved UPS (ARUPS)

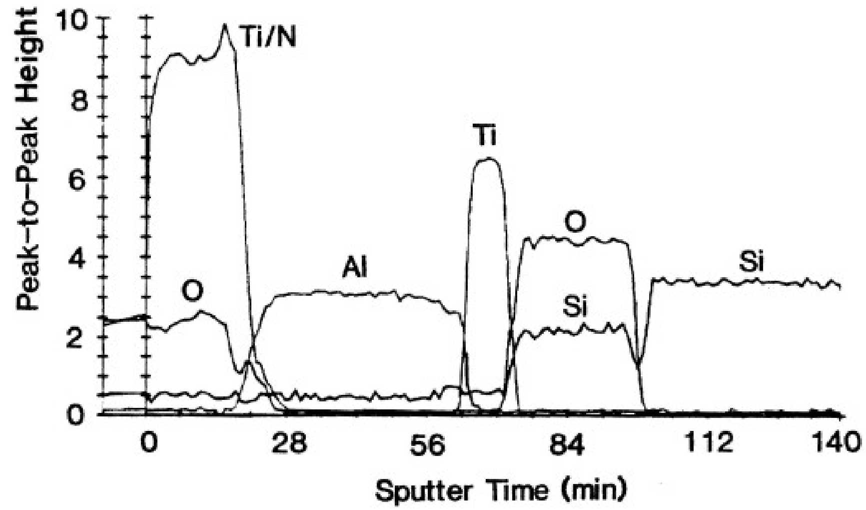


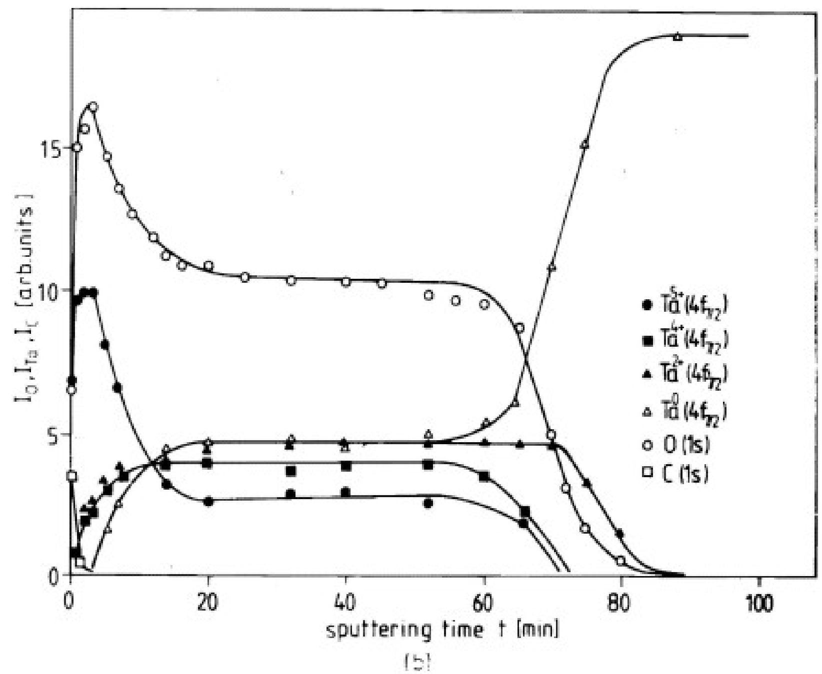
Ertl/Küppers, Low energy electrons and surface chemistry, VCH

Depth profiling

Sputtering during AES analysis







Briggs/Seah, Practical Surface Analysis, Wiley